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STRENGTHENING OF OXIDATION RESISTANT

MATERIALS FOR GAS TURBINE APPLICATIONS

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TABLE OF CONTENTS

LIST OF TABLES

iv

LIST OF TABLES (Cont'd)

LIST OF FIGURES

I. SUMMARY

Two candidate materials for development for use in gas turbine engines are hot pressed silicon carbide and hot pressed silicon nitride. These materials, though brittle and, consequently, deficient in impact resistance have high mechanical strength and oxidation resistance at expected turbine operating temperatures. Therefore the merits of these materials make it worthwhile to try to overcome their limitations.

In well-made polycrystalline ceramics, fracture originates at surface flaws. Compressive surface layers are effective in raising the nominal stress at which these surface flaws act to cause failure, thus increasing the mechanical strength of the material.

Attempts were made to form compressive surface layers on hot pressed silicon carbide and hot pressed silicon nitride at 1590°K (2400°F) in order to improve their impact resistance at that temperature.

Two processes appeared to be especially attractive. One was quenching of silicon carbide, the other was carburizing silicon nitride.

Compressive surface stresses were generated on quenched silicon carbide. However, thermal shock fracture and alteration of surface layers through reaction with air or carbon monoxide prevented the improvement in impact resistance except for small cylindrical rod specimens. It is believed that these problems can be overcome by judicious selection of quenching process variables, specimen size and shape, and the severity of quench.

Silicon nitride was carburized by packing in carbon black and heating to an elevated temperature. Compressive surface stresses were generated at 1590°K (2400°F) and some impact resistance values exceeded the short term goal of six inch pounds. However, impact resistance values for carburized silicon nitride were inconsistent with some being lower than control values. The carburizing process makes a new, unidentified phase(s) or compound at the surface of silicon nitride. The expected presence of silicon carbide in the surface was not detected. Consequently, the carburizing process is not well understood and consistent improvement in impact resistance must await better understanding of the process.

1

II. INTRODUCTION

A. Background

Metal alloys are presently satisfying the demands of aircraft turbine engines. These superalloys, which have sufficient strength and oxidation resistance, are used for hot components such as turbine blades and stator vanes. However, future developments in engine technology are expected to push operating temperatures much higher and substitute materials are being sought.

Two candidate materials for future development are hot pressed silicon carbide and hot pressed silicon nitride. These refractory materials have high mechanical strength and excellent resistance to oxidation[1] at expected operating temperatures which will approach 1590°K (2400°F) for stator vanes. However, these materials are very brittle and, consequently, lacking in resistance to mechanical impact. Nonetheless, the merits of silicon carbide and silicon nitride make it appear worthwhile to attempt to overcome their limitations.

In polycrystalline ceramics, subjected to external forces, fracture originates at surface flaws. Compressive surface layers increase the nominal stress at which these flaws act to cause failure, thus improving the mechanical strength of brittle ceramic materials. This approach has been demonstrated to be effective for alumina,[2-16] titania,[2,3] steatite,[3] forsterite,[3] spinel,[3,5] magnesia,[3,6] silicon carbide,[16] and zircon porcelain[16] ceramics. The compressive surface layers can be used to obtain substantial improvements in flexural strength, tensile strength, resistance to thermal shock, impact resistance, and delayed fracture performance. Among the methods for forming compressive surface layers at an elevated temperature are:

1. Mismatching of thermal expansions or contractions of the surface layer and the underlying body.

2. Quenching.

In the first method, the temperature at which the surface layer is formed can be selected so that regardless of whether the thermal expansion of the surface layer is higher or lower than that of the body, the surface layer is in compression at some predetermined elevated temperature.

2

In the second method, the compressive surface layers formed by quenching are retained practically indefinitely at temperatures at which creep or plastic flow of the ceramic does not occur.

B. Program Objectives

The main objective of this program was to improve the high temperature impact resistance of silicon carbide and silicon nitride polycrystalline ceramics. The short range goal for impact resistance was six inch pounds at 1590°K (2400°F); the long range goal was two to five foot pounds. The improvements were sought through methods which result in compressive surface layers at that temperature. These methods were:

1. Formation of silicon nitride surface layers on silicon carbide at temperatures above 1590°K (2400°F). Compressive stresses form in the surface layers because of the greater thermal contraction to the temperature of 1590°K (2400°F) of the underlying silicon carbide which has a higher thermal expansion coefficient than silicon nitride.

2. Formation of compressive surface layers on silicon carbide by quenching. During quenching, the surface of the body is placed initially under a tensile force and the core is in compression. If the temperature of the core is high enough, creep will occur during the first few moments and this will relieve some or all of the core compressive stress and the surface layer tensile stress. Since the surface is already relatively cold, continued cooling below the creep-temperature range and contraction of the core results in the surface layers being put in compression.

3. Formation of compressive surface layers using the thermal expansion relationship of α- and β- forms of silicon carbide. Compressive stresses form at 1590°K (2400°F) in surface layers of β-silicon carbide vapor deposited at temperatures below 1590°K (2400°F) on α-silicon carbide because of the thermal expansion of the underlying α-silicon carbide which is lower than that for β-silicon carbide.

4. Formation of random silicon carbide surface layers on oriented silicon carbide. This method requires forming an oriented body of

α-silicon carbide with its a-axis parallel
to the surfaces. If a randomly oriented
silicon carbide layer is placed on this body
at high temperatures, the surface would be
in compression at 1590°K (2400°F) because
of the greater thermal contraction of the
underlying body (a-axis) than that for the
surface layer.

5. Formation of β-silicon carbide at about
1090°K (1500°F) on silicon nitride.
Compressive stresses form in the β-silicon
carbide surface layers at 1590°K (2400°F)
because of the greater thermal expansion of
the surface layers than that of the under-
lying body.

C. Scope of the Program

Two materials, hot pressed silicon carbide and
hot pressed silicon nitride, at least 95% dense, were
treated according to the methods listed above. Cylindrical
and rectangular rod specimens were treated and evaluated
by the slotted rod test at room temperature and at
elevated temperatures. Rectangular bar specimens were
treated and evaluated by Charpy impact test at room
temperature and at 1590°K (2400°F). In some cases,
flexural strengths were determined in order to augment
the evidence from rod tests and impact tests.

In accord with NASA policy, the units used in this
report are SI units with secondary units given in the
English system. Original measurements were made in
English or metric units and converted for reporting
purposes.

III. PROCEDURES

A. Materials

1. Silicon Carbide

The silicon carbide used in this work was produced
by Alfred Ceramic Enterprises. This was hot pressed
material with a grain size in the range of 3-5 μm. It
was about 98% silicon carbide, the remainder being mostly

a proprietary sintering aid. The bulk density was
3120 kg/m^3 (195 lb/ft^3) and the open pore volume was
of the order of 0.2%. The bulk density was 97.2% of
theoretical density, 3210 kg/m^3 (200 lb/ft^3).

An electron micrograph of a polished and electro-
lytically etched surface of the silicon carbide is shown
in Figure 1.

Both cylindrical and rectangular rods were machined
from this material. The cylindrical rods had diameters
of about 2.5 mm (0.1 in.); prismatic rods were 3.8 mm x
3.8 mm x 57.1 mm (0.15 in. x 0.15 in. x 2.25 in.).

Rectangular impact test bars were machined with the
dimensions: 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in.
x 2.25 in.). Machining was done with a diamond blade
and the cut surfaces were usually left as-machined with
no refinishing. The edges were slightly rounded manually.

2. Silicon Nitride

Silicon nitride was obtained from the Norton Company.
It was hot pressed material containing a proprietary
sintering aid. The grain size is in the neighborhood of
1 μm. The bulk density is 3190 kg/m^3 (199 lb/ft^3) and the
open pore volume is negligible, of the order of 0.2%.
The average flexural strength of six rods, 2.03 mm diameter
(0.08 in.), determined by four point loading on a one
inch span is 1036 MN/m^2 (150,200 psi) at room temperature.

Specimens for rod tests and impact tests were prepared
as described in the previous section.

Some preferred orientation existed in this material.
This observation for similar material had been reported
by Lange[17] and his procedure was duplicated here. X-ray
diffraction patterns were obtained from surfaces parallel
and perpendicular to the hot pressing direction. These
patterns show that x-rays diffracted from planes parallel
to the c-axis (hk0) had a greater relative intensity from
the surface perpendicular to the hot pressing direction.
Also, x-rays diffracted from planes intercepted by the
c-axis (hkl) had a greater relative intensity from the
surface parallel to the hot pressing direction. Evidently
the c-axis had a preferred orientation perpendicular to
the hot pressing direction.

Figure I – Hot Pressed Silicon Carbide. Electronmicrograph of polished and etched surface (8380X). The grain size is in the range of I–5 μm.

B. Methods of Evaluation

1. Rod Tests

<u>Room temperature rod tests</u>

The relative magnitudes of the stresses in the surfaces of treated specimens can be estimated by slotted rod (or bar) tests. In these tests, restraints are removed by slotting a rod or bar and any resultant deformation indicates the sign and relative magnitude of the surface forces. If the ends of the slot move apart (open), tensile forces were present in the surface layers. If the ends of the slot come together (close), compressive forces were present.

In similar specimens with surface layers of similar thickness and elastic modulus, the amount of opening or closing increases with increasing stress. Also, the amount of opening or closing is directly proportional to the square of the length of the slot. A sketch of a typical rod test is shown in Figure 2.

The technique for conducting the slotted rod test was described in the literature.[18] In this work, a slot 0.30 mm (0.012 in.) or 0.76 mm (0.030 in.) wide and 28 mm-30 mm long (1.10 in.-1.18 in.) was made. Optical measurements of the slot displacement were made using oblique lighting and a microscope with a 40 mm objective and a 10X eyepiece containing a ruled disc.

Since two slot widths were used and because specimen dimensions varied, a standardized slot deflection was sometimes calculated for rectangular rods. The standardizations were made by taking into account the actual dimensions of the piece, the actual width of the slot, and the length of the slot.

The slot deflection was calculated from the bending moment acting in a prismatic cantilever beam. The general expression for beam deflection is:

$$\frac{d^2\delta}{dx^2} = \frac{M}{EI}$$

where M is the bending moment acting at a section at a position x, E is the elastic modulus and I is the moment of inertia of the cross sectional area about its neutral
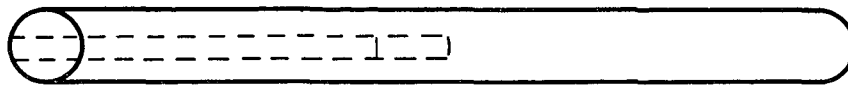
Before Slotting

Tensile Stresses Relieved

Compressive Stresses Relieved

Figure 2 – Rod Test

axis. Since the moment M is not a function of x, distance along the beam, iterative integration for $L > x > 0$ yields:

$$\delta = \frac{ML^2}{2EI}$$

where L is the beam length, in this case, the slot length. The total deflection is:

$$D = 2\delta = \frac{ML^2}{EI}$$

An estimate of the moment M is not always available but it can be written that:

$$D = k\frac{L^2}{I}$$

A correction can then be calculated by forming the ratio

$$\frac{D_1}{D_2} = \frac{L_1^2\,I_2}{L_2^2\,I_1}$$

The moment of inertia I is the moment of the cross sectional area of one segment of the slotted rod about its neutral axis. The height of this area is perpendicular to the plane of the slot, hence it is one-half of the difference between the thickness of the rod, measured perpendicularly to the slot plane, and the slot width, taken as the width of the slotting blade.

A standard configuration was assumed in which the rod thickness is 0.136 in. (an average value), the slot length L is 1.1875 in. and the blade width is 0.012 in. The corrected slot deflection was then computed by:

$$D_c = 7.94436\,\frac{D}{L^2}\left[\frac{(2t)^2}{2t - 2s}\right]$$

where D was the measured deflection, 2s was the width of the slotting blade and 2t was the thickness perpendicular to the slot plane.

A correction was sought initially in order to compare rod test results using two different thicknesses of slotting blade. The rod thickness, in the case of rectangular specimens, varied within ±15% and so this was also an important factor.

High temperature rod tests

In order to verify the predicted behavior according to the treatment methods, a high temperature rod test was conducted. In this test, slot width was measured at various temperatures and the deflection, as an indicator of the state of surface forces, could be determined at 1590°K (2400°F). To conduct this test a furnace was assembled which consisted of a bayonet type silicon carbide resistance heating element in insulating fire-clay brick. A sight hole passed through the insulation and between the spirals of the heating elements. Rod test specimens were placed along the hollow axis of the heating element so that the slotted tip could be viewed through the sight hole with a long focal length microscope. A thermocouple was placed from the opposite end of the bayonet element to within 3 mm (0.12 in.) of the slotted tip. The temperature difference over the test length was found to be ±15°K (27°F) at a holding temperature of 1560°K (2350°F).

Figure 3a is a photograph of the high temperature rod test set-up and Figure 3b is a photograph showing the slotted rod mounted in a vitreous silica holder for insertion along the axis of the heating element.

2. Impact Test

The basic impact machine was a Bell Telephone Laboratories Type machine supplied by Satec Systems, Inc. It was equipped for the Charpy mode of impact testing with a 1.36 joule (12 in-lb) or a 2.71 joule (24 in-lb) hammer and with a 101.6 mm (4 in.) specimen span. Most of the testing was done with the smaller hammer.

The impact machine was modified for high temperature tests by first removing the specimen supports and anvils. Then an inductively powered furnace was installed between the hammer supports. The furnace was locked into a water cooled frame which was securely bolted to the base of the impact machine. The furnace was a fireclay brick channel with various insulating materials which ran on line with the swing of the hammer. The modified machine is shown in Figure 4. Graphite plates, 38.1 mm (1.5 in.) apart, were firmly supported on each side of the channel as shown in Figure 5. These plates were the heating elements; they were energized by pancake induction coils in close proximity to their exterior surfaces. In addition, each plate rigidly held a silicon carbide insert which served
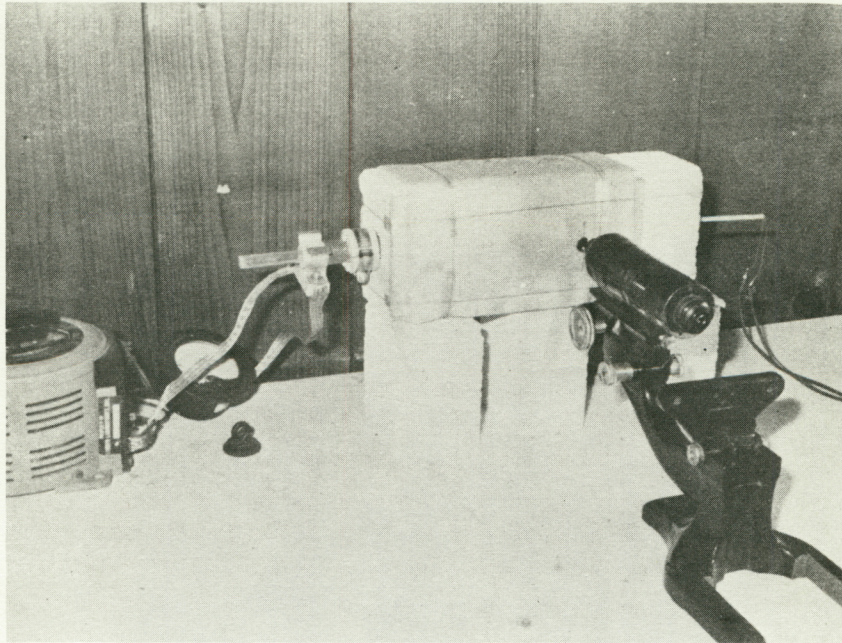
(a)
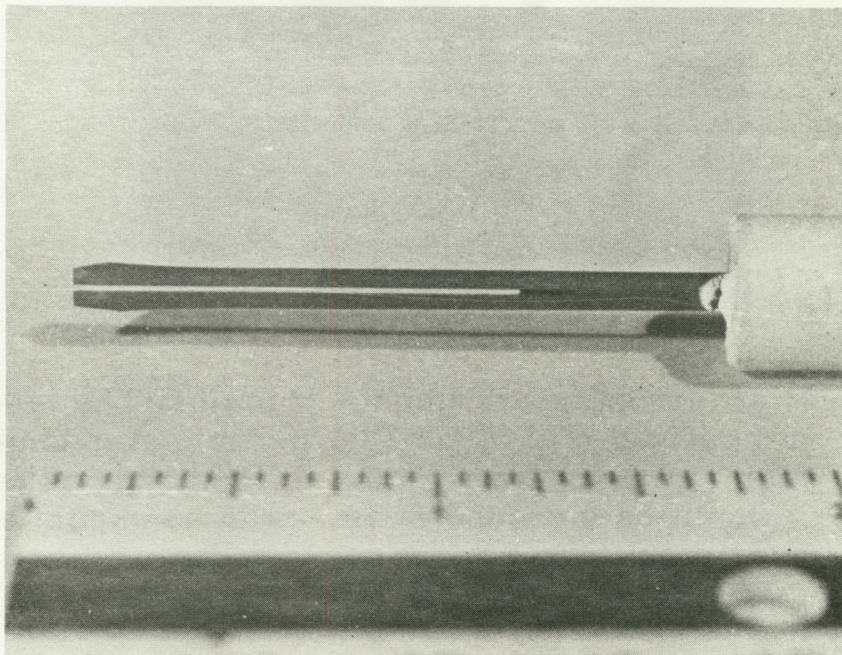
(b)

Figure 3 – The High Temperature Rod Test Set-Up (a), and a
Slotted Rod Mounted in a Vitreous Silica Holder for
Insertion Along the Axis of the Heating Element (b).

11
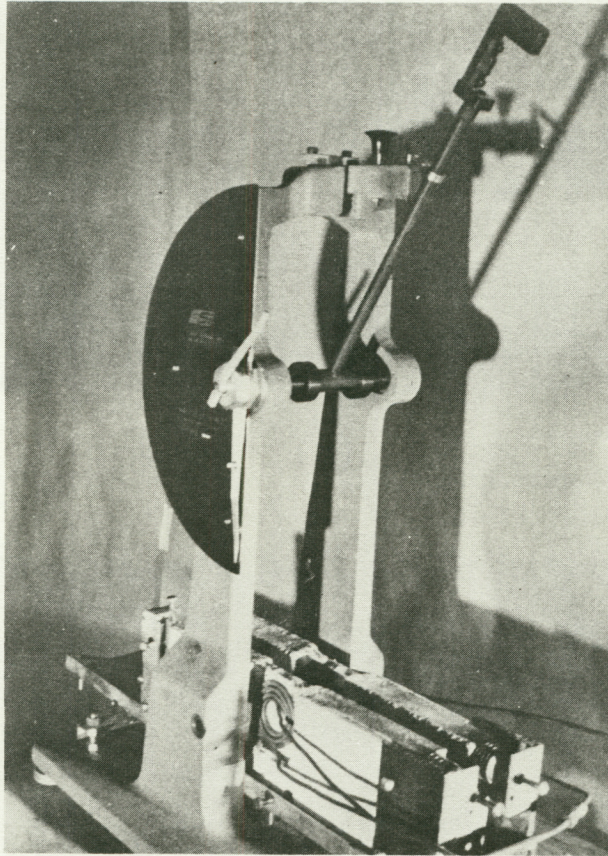
Figure 4 – High Temperature Impact Machine. The machine is a modified BTL type Charpy impact machine. The high temperature furnace lid has been removed as it would be a second or two prior to impacting a specimen.

12

Figure 5 – Close-Up of the High Temperature Impact Machine. The graphite heating elements, which also hold the specimen support and anvil, and the pancake induction coils are shown.
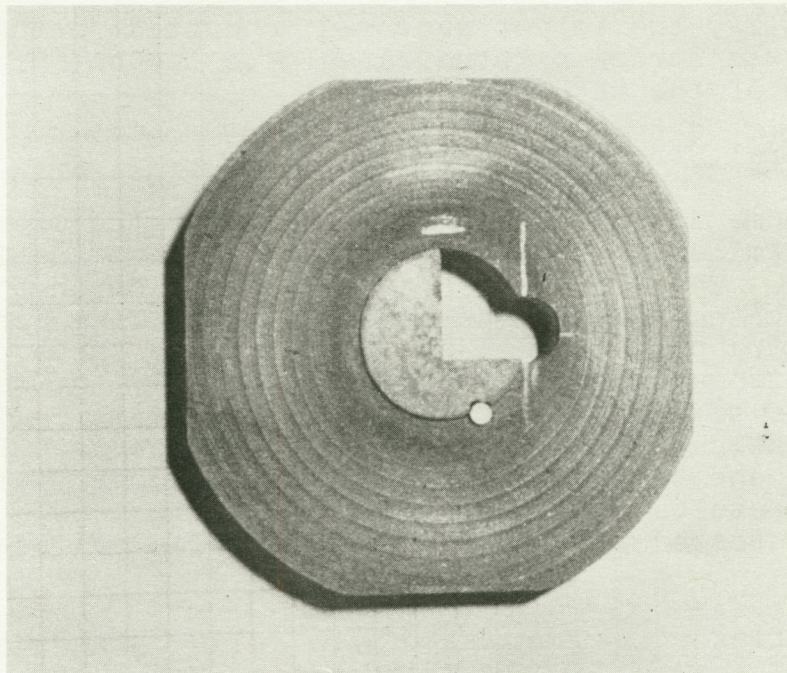
Figure 6 – Graphite Plate Heating Element for the High Temperature Impact Machine. The plate rigidly holds a silicon carbide insert which is also pinned in place and which serves as support and anvil for the impact test piece.

13

as support and anvil for the impact test specimen. One such plate is shown in Figure 6. The furnace was equipped for inert gas purging to prolong the life of the plates. The power supply was a 2.5 kW or 5.0 kW high frequency generator.

For the high temperature impact test, the furnace with a specimen in place was heated rapidly to 1590°K (2400°F) and then held there for one to five minutes. The temperature was monitored with an optical pyrometer that was sighted on the back surface (tensile surface) of the bar specimen. To impact test, the furnace lid was removed, the power was turned off and the hammer was released. This was all done quickly, say, within two or three seconds.

The impact resistance was measured directly by the machine in foot-pounds as the energy lost by the hammer in breaking the specimen. A correction was made for windage loss but none was made for toss factor. The impact resistance was recorded as an energy in joules (in-lb in English units) for a standard nominal test piece, as described earlier, without conversion to stress or energy density to account for specimen dimensions. This procedure was satisfactory for internally consistent data obtained from standard size specimens.

Usually, the impact test was conducted so that the blow was struck perpendicularly to the hot pressing direction of the material.

3. Flexural Strength

In some instances the flexural strengths of materials were determined in order to augment rod test and impact test data. The room temperature flexural strength was measured using four point loading with rolling contacts at the third points and a one inch span or three point loading with a one-half inch span. Usually the measurements were made at about 20% relative humidity. The loading rates were chosen so that specimens usually failed in one to five minutes. These methods yield reliable results with small standard deviations. Materials tested were in the form of solid cylinders or bars.

The flexural strengths of the solid cylinders under four point loading at the third points were computed from:

$$\sigma = \frac{1.70 \; Pl}{D^3}$$

14

in which σ was the tensile stress in the outermost
material, P was the total load, l was the total span,
and D was the diameter. Only cylinders were tested in
this manner.

The equation for three point loading of rectangular
bars was:

$$\sigma = \frac{3}{2} \frac{Pl}{bh^2}$$

in which σ was the tensile stress in the outermost
material, P was the total load, l was the total span,
b was the width of the specimen, and h was the height,
or thickness, of the specimen.

The equation for three point loading of cylinders
was:

$$\sigma = 2.55 \frac{Pl}{D^3}$$

in which the symbols were defined as above.

Usually the load in flexural strength testing was
applied perpendicularly to the hot pressing direction.

4. X-ray Diffraction Analysis

The x-ray diffraction analyses were performed using
a Norelco diffractometer to determine preferred orientation
and phase compositions of the surfaces of solid specimens.

5. Electron Microscopy

The microsctructure of the hot pressed silicon
carbide was determined from electron micrographs prepared
by William Corbett of the Pennsylvania State University
using a Phillips E.M. 300 electron microscope. Carbon
replica techniques were used to prepare replicas from
polished and etched surfaces.

Satisfactory micrographs of silicon nitride were
not obtained because of the inability to obtain a suitable
etch.

C. Evaluation of the Modified Impact Machine

A standard test was selected which used alumina
specimens and the unmodified machine, that is, with its

usual specimen supports and anvils. The standard specimens were ALSIMAG 614[*] polycrystalline 96% alumina rods, 7.62 mm (0.3 in.) in diameter and in this test 127 mm (5 in.) long. This material was an excellent standard because it has been well characterized as to its mechanical strength behavior in extensive research programs at this laboratory.[2-15]

Nine specimens were tested and the results are listed in Table I. The average impact resistance was 0.1953 joules (1.729 in-lb); the standard deviation was 0.0258 joules (0.2282 in-lb) which yielded a coefficient of variation of 13.2%.

A standard test was also selected to ascertain the variability introduced by the high temperature modifications. The test used the same alumina specimens but 57.2 mm (2.25 in.) in length. Also the furnace and specimen supports and anvils were in place but at room temperature. The test span was 38.1 mm (1.5 in.).

Nine specimens were tested and the results are listed in Table II. The average impact resistance was 0.1940 joules (1.717 in-lb) and the standard deviation was 0.0223 joules (0.197 in-lb) which yielded a coefficient of variation of 11.5%. It was noted that these values are very close to those for the unmodified machine.

In view of these results it was concluded that the coefficient of variation to be expected when using the modified machine was about 12% and the variability was about the same as that found for the unmodified machine. In other words, the modifications did not introduce additional variability of room temperature impact test results.

The ability of the Charpy impact test to distinguish strengthened materials was investigated. ALSIMAG 614 alumina rods 7.26 mm (0.3 in.) diameter x 127 mm (5 in.) long or -x 57.2 mm (2.25 in.) long were quenched from $1770°K$ $(2730°F)$ into silicone with a viscosity of 350 $x10^{-6}$ m^2/sec (350 centistokes). The treated specimens were impact tested at room temperature in both the unmodified and high temperature machine. The results are listed in Table III along with the averages for untreated specimens reported in Tables I and II.

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[*] American Lava Corporation

TABLE I

Room Temperature Impact Resistance of
Standard Alumina Specimens

Charpy impact test; unmodified machine; 1.36 J (12 in-lb) hammer; 101.6 mm (4 in.) span; ALSIMAG 614 polycrystalline alumina rods, 7.62 mm (0.3 in.) dia. x 127 mm (5 in.) long

Impact Resistance joules	Impact Resistance in-lb
0.1792	1.586
0.1792	1.586
0.1773	1.569
0.1785	1.580
0.1792	1.586
0.1773	1.569
0.2367	2.095
0.2278	2.016
0.2228	1.972
Average 0.1953	1.729

Standard Deviation - 0.0258

Coefficient of variation - 13.2%

TABLE II

Room Temperature Impact Resistance of
Standard Alumina Specimens Tested in the
High Temperature Impact Machine

Charpy impact test; modified machine; 1.36 J (12 in-lb)
hammer; 38.1 mm (1.5 in.) span; ALSIMAG 614 polycrystalline
alumina rods, 7.62 mm (0.3 in.) dia. x 57.2 mm (2.25 in.)long

Impact Resistance joules	Impact Resistance in-lb
0.1726	1.528
0.1807	1.599
0.1961	1.736
0.1862	1.648
0.1786	1.581
0.1988	1.760
0.1731	1.532
0.2257	1.998
0.2339	2.070
Average 0.1940	1.717

Standard Deviation - 0.0223

Coefficient of variation - 11.5%

TABLE III

Room Temperature Impact Resistance of Alumina Quenched from
1770°K (2730°F) into Silicone (viscosity = 3.50×10^{-4} m^2 sec^{-1} or 350 cs)

Charpy impact test; 1.36 joules (12 in-lb) hammer
ALSIMAG 614 polycrystalline alumina rods, 7.62 mm (0.3 in.) dia.

Treatment	Impact Test Span	No. Specimens	Average Impact Resistance		% Increase
			joules	in-lb	
Unmodified impact machine					
As-received	101.6 mm (4 in.)	9	0.1953	1.729	
Quenched in silicone	101.6 mm (4 in.)	3	0.4403	3.898	125%
Modified impact machine					
As-received	38.1 mm (1.5 in.)	9	0.1940	1.717	
Quenched in silicone	38.1 mm (1.5 in.)	3	0.5195	4.598	168%

The quenched rods had impact resistances of 0.4403 joules (3.898 in-lb) as measured by the unmodified machine and 0.5195 joules (4.598 in-lb) as measured by the modified machine and these values represent more than doubling the impact resistance. Previous work[13] with the same material similarly treated but with a smaller diameter, 3.20 mm (.126 in.), showed increases in impact resistance of the same amount. In that work impact resistance was evaluated by the drop weight method instead of the Charpy method.

The significantly higher impact test results for the treated alumina amply demonstrated the ability of the Charpy mode of testing, using unnotched specimens, to distinguish materials strengthened by compressive surface layers. This was true for the modified machine as well as the unmodified machine.

IV.   RESULTS AND DISCUSSION OF RESULTS

A.   Silicon Nitride Surface Layers on Silicon Carbide

If a silicon nitride surface layer is placed on a silicon carbide body at a high temperature, compressive stresses will form in the surface layer at lower temperatures because of the greater thermal contraction of the underlying silicon carbide body than the thermal contraction of the silicon nitride surface. Typically, over the range 290°-1470°K (60°-2190°F) silicon carbide has a coefficient of thermal expansion of 5.0×10^{-6} m/m°K (2.78×10^{-6} in/in°F) whereas silicon nitride has a coefficient of thermal expansion of 2.78×10^{-6} m/m°K (1.54×10^{-6} in/in°F).[19]

1.   CVD Silicon Nitride

Silicon nitride was chemically vapor deposited on a silicon carbide rectangular rod. The reactants were silane (SiH_4), ammonia, and hydrogen. The reaction was conducted in a cylindrical graphite chamber enclosed in a shell of vitreous silica at a pressure slightly above atmospheric pressure. The graphite served as the heating element and it was inductively powered. In thirty minutes at 1720°K (2640°F) a layer 25-50 μm (1-2 mils) thick was deposited. The room temperature rod test result was that the slot closed 50 μm (2 mils) indicating that compressive forces

20

were formed in the surface layer. This was the anticipated result.

The vapor deposited silicon nitride surface layer was not uniform and not of a quality which could be expected to improve the strength of the underlying body. Further work was done with chemical vapor deposition to deposit more uniform and heavier coatings. In a number of experiments, relative concentrations of reactants and the total flux of reactants were varied over wide ranges but improved deposits were not obtained. The deposition temperature was varied between narrow limits and this also was ineffective in improving surface deposits.

2. Pack Nitriding

Another feasible method of making silicon nitride surfaces on silicon carbide was pack nitriding. It involved packing the silicon carbide in silicon nitride powder in a closed container and heating to a high temperature. A silicon carbide rod was packed in silicon nitride powder in a closed graphite tube and heated to 2070°K (3270°F) for 0.5 hour. The rectangular rod showed dimensional increases of 15 μm (0.6 mils) across one pair of faces and 71 μm (2.8 mils) across the other pair of faces. The room temperature rod test result was that the slot, 305 μm wide (12 mils) and 32 mm long (1.25 in.), closed 51 μm (2 mils) indicating that compressive surface forces had been formed. Other packing experiments were conducted at a higher temperature in order to obtain more and deeper reaction. At 2170°K (3450°F) there was excessive reaction among the carbide, nitride, and graphite which resulted in a fused mass and ruined specimens.

A treated surface from the rod test specimen was examined by x-ray diffraction. The strongest diffraction peaks for silicon carbide and silicon nitride very nearly overlap. However, a fairly strong indication of diffraction from the (210) planes of β silicon nitride was evident. Also there was a diffraction peak that is characteristic of the (111) plane of silicon.

Another silicon carbide rod was pack nitrided at 2070°K (3270°F) for a longer period of time. The room temperature rod test on this specimen yielded a null result, that is, the slot did not close or open. No further experiments were conducted because of emphasis on other parts of the program.

3. Nitrided CVD Silicon

Another method for making silicon nitride surfaces was investigated. This method involved vapor plating silicon on a silicon carbide rod using the reactants, hydrogen and silane (SiH_4), and then converting the silicon to silicon nitride using ammonia. The silicon was deposited at 1270°K (1830°F). It was then held at 1720°K (2640°F) in a stream of ammonia for 2.8 hours and at 1750°K (2690°F) for 1.5 hours. The coating so formed was not uniform. It consisted in part of prominent nodules. Because of the generally poor nature of the coating, the rod test was not done and no further work with this method was done.

4. Reaction Sintered Silicon Nitride Coating

In this method silicon carbide rod specimens were coated with a compound of silicon nitride and silicon powders. The coating was fired above the melting point of silicon in an atmosphere containing nitrogen. It was expected that the silicon would be converted to nitride thus forming an adhering dense coating. Coatings were compounded with 5.4%, 14.4% and 21.7% silicon with the remainder as silicon nitride. Benzene was used as the vehicle. Coated rods were fired at 1720°K (2640°F) for one hour in ammonia.

All of the resulting coatings appeared to be only partially nitrided; grains with metallic luster were visible. Also, whiskers assumed to be silicon nitride were deposited at the base of each specimen. The 5.4% and 21.7% silicon coatings did not adhere. The 14.4% silicon coating did adhere but parts of it could be easily flaked off. The rod with the 14.4% silicon coating was tested by the rod test with the result that the slot did not open or close. No further work with this method was done.

5. Discussion

The rod test result from the chemical vapor deposited silicon nitride on silicon carbide and the rod test result from the pack nitrided silicon carbide indicated that this method of forming compressive surface layers is potentially useful. The method has not been proven conclusively because of experimental difficulties in forming well developed surface layers of silicon nitride. Nonetheless, the attractive potential of forming a surface layer on silicon carbide with some degree of compressive

22

stress from room temperature to temperatures well above the projected use temperature still remains.

Evidently, developments in process control are needed in order to deposit well-formed silicon nitride surface layers and to form a nitrided surface on silicon carbide by the pack technique. Also, process developments for nitriding vapor deposited silicon, say by successive deposition and nitridation of very thin layers, and for reaction sintered silicon nitride surface layers, say by utilizing an oxide interlayer (pre-oxidized silicon carbide body), are needed.

B. Quenched Silicon Carbide

When silicon carbide is quenched from a temperature where it deforms by creep, compressive surface layers are formed. During quenching, the surface of the body is placed initially under a tensile force and the core is in compression. The temperature of the core is high enough during the first few moments to permit creep which relieves some or all of the core compressive stress and the surface layer tensile stress. Since the surface is already relatively cold, continued cooling below the creep-temperature range and contraction of the core results in the surface layers being put in compression.

1. Experimental Procedures

Silicon carbide specimens were quenched individually from a cylindrical graphite chamber that was brought to the quenching temperature by induction heating.

Quenching media were silicone fluids and forced helium.

When rectangular impact bars were being heated the quenching furnace was continuously purged with helium to inhibit deterioration through oxidation. Rod test specimens were sometimes placed in a purged furnace but usually this was unnecessary because the heating periods were very short.

Temperatures were read on a reflected image from either a sight hole in the graphite chamber wall or directly on the test specimen using an optical pyrometer.

Some specimens were placed in a cold furnace and then heated to the quenching temperature. This procedure was replaced because it extended the time interval during which the specimen was at high temperatures and increased the likelihood of deterioration. Instead, specimens were placed in a furnace at several hundred degrees below the quenching temperature and then heated rapidly. It was determined that this procedure did not introduce damage due to thermal up-shock. In all cases, the quenching temperature was held for a sufficient time to reach a uniform temperature throughout the specimen.

2. Rod Test Results

Quenched silicon carbide rectangular rods were slotted with a 0.30 mm (0.012 in.) thick diamond cut-off blade and the slotted rod tip deflection was measured. The quenching temperature varied from 2400°K (3860°F) to 2670°K (4350°F) and the quenching media were silicone fluids with viscosities of 20×10^{-6} m^2/sec and 100×10^{-6} m^2/sec. In all cases the slotted rod tip deflection was negative and large and this indicated that high compressive surface forces had been induced. The data are given in Table IV. There did not seem to be any advantage of one silicone fluid over the other but the greatest deflection was obtained when the more viscous fluid was used. There was no correlation between quenching temperature and slotted rod tip deflection. However, with both fluids, the quenching temperature that gave the highest deflection was 2500°K (4040°F).

The silicon carbide specimen that had been quenched from 2670°K (4350°F) into silicone with a viscosity of 100×10^{-6} m^2/sec was subjected to the high temperature rod test in which the specimen was heated to 1650°K (2510°F) and then the slotted rod tip deflection was measured as the piece cooled slowly. This specimen to start had a negative tip deflection of 0.221 mm. The slotted rod tip deflection did not change over the temperature range studied. This was the expected result if stress relaxation processes did not occur. It showed that quenched rods can be expected to retain their compressive surface stresses at operating temperatures of 1590°K (2400°F).

Silicon carbide controls that had not been quenched or otherwise thermally treated were tested by both the room temperature and the high temperature rod tests. In both cases no slotted rod tip deflection was detected.

24

TABLE IV

Room Temperature Rod Tests on Quenched Silicon Carbide

Positive deflection indicates tensile surface forces, negative deflection indicates compressive surface forces

Quenching Temperature		Slotted Rod Tip Deflection(a)

Quenching medium: silicone, $\eta = 20\text{x}10^{-6}\ m^2/sec$

2400°K	3860°F	-0.145 mm
2500	4040	-0.229
2500	4040	-0.147
2600	4220	-0.048

Quenching medium: silicone, $\eta = 100\text{x}10^{-6}\ m^2/sec$

2400°K	3860°F	-0.193 mm
2500	4040	-0.259
2600	4220	-0.185
2670	4350	-0.221

(a) All deflection values are standardized for slot width, length, and specimen dimensions and corrected for deflection of untreated control material, when applicable.

3. Impact Test Results

Silicon carbide impact test bars were quenched from various temperatures ranging from 2300°K (3680°F) to 2740°K (4470°F). The quenching medium was also varied.

The first group of bars, quenched from 2500°K (4040°F) into silicone fluid with a viscosity of 100×10^{-6} m²/sec had cracks running from one end axially down one surface. These bars were not impact tested but one of them was slotted at about 12 mm (0.047 in.) from one side of the bar. The slot closed 0.10 mm (0.004 in.) and this indicated that compressive surface forces had been generated.

Subsequently, silicon carbide impact test bars to be quenched from 2500°K (4040°F) and above were end-dipped in a slurry of silicon carbide powder and thinly coated with spray graphite to reduce the tendency for crack formation. With spray graphite alone cracking continued. With end dipping and spray graphite some specimens survived, apparently without cracking.

A number of quenched bars were obtained and their impact resistances and the impact resistances of some controls are given in Table V.

Two bars were quenched in still air. They had an average impact resistance at 1590°K (2400°F) of 0.228 joules (2.02 in-lb). This value is in the range of the impact resistance of controls at 1590°K (2400°F) which average 0.280 joules (2.48 in-lb).

Several bars were quenched from 2270°K (3630°F) in forced helium but only one was obtained which did not have an axial crack along one surface. This bar had an impact resistance at 1590°K (2400°F) of 0.227 joules (2.01 in-lb), a value not significantly different from those of the controls.

Two bars were quenched in silicone fluid with a viscosity of 100×10^{-6} m²/sec. The first was quenched from 2500°K (4040°F) and it had a 1590°K (2400°F) impact strength of only 0.055 joules (0.49 in-lb). The specimen had been weakened instead of strengthened. Quenching from a higher temperature was considered as a means of getting impact resistance improvement. Therefore, a bar was quenched from 2740°K (4470°F). This bar had a

26

TABLE V

Impact Resistance of Quenched Silicon Carbide
Impact Test Bars

Quenching Temperature		Impact Resistance[a]			
°K	°F	300°K (R.T.)		1590°K (2400°F)	
		joules	in-lb	joules	in-lb
Controls					
		0.519[b]	4.60	0.286	2.53
		0.146[b]	1.30	0.220	1.95
				0.490	4.33
				0.127	1.12
				0.353	3.12
				0.244	2.16
				0.255	2.26
				0.266	2.35
Average		0.332	2.95	0.280	2.48
Quenched in still air					
2500	4040			0.207	1.83
2500	4040			0.249	2.21
Average				0.228	2.02
Quenched in forced helium					
2270	3630			0.227	2.01
Quenched in silicone: $\eta = 100 \times 10^{-6}$ m^2/sec					
2500	4040			0.055	0.49
2740	4470			0.139	1.23
Quenched in silicone: $\eta = 350 \times 10^{-6}$ m^2/sec					
2300	3680			0.087	0.77
2400	3860			0.038	0.34
2400	3860			0.186	1.64
2400	3860			0.211	1.87
2400	3860			0.133	1.18
Average				0.142	1.26

(a) Charpy impact test; 1.36 J (12 in-lb) hammer except
as noted; 38.1 mm span (1.5 in.); test bars nominally 6.35 mm
x 6.35 mm x 57.1 mm (0.25 in. x 0.25 in. x 2.25 in.)
(b) Impact test as in (a) but with 2.71 J (24 in-lb) hammer.

high temperature impact resistance of 0.139 joules
(1.23 in-lb). Although this was greater than the
previous result, it still does not represent improved
impact resistance.

A more viscous quenching medium, silicone fluid
with a viscosity of 350×10^{-6} m^2/sec, was also tried.
One bar quenched from 2300°K (3680°F) had a 1590°K
(2400°F) impact strength of 0.087 joules (0.77 in-lb).
A group of four bars quenched from 2400°K (3860°F) had
an average high temperature impact resistance 0.142
joules (1.26 in-lb). These results did not indicate
improvement in impact resistance over that for untreated
bars.

The back surfaces or tensile surfaces of a group
of impact test bars were polished using 6 μm diamond
paste on a cast iron lap. Some of these were quenched
from 2400°K (3860°F) in silicone fluid with a viscosity
of 350×10^{-6} m^2/sec and some were used untreated as
controls. The impact resistances at room temperature
and at 1590°K (2400°F) were determined and they are
given in Table VI. The average impact resistances of
the controls were about the same as those for controls
that had not been polished. The average impact resistance
of the polished and quenched bars was lower than those
for bars that were as-machined and quenched.

Most of the quenched bars tested by impact had
fracture surfaces that exhibited a sharp step perpen-
dicular to one of the surfaces. This feature indicated
that those specimens probably had the same type of
crack running axially down one side that had been observed
and described previously. In these cases, the crack was
finer and not observable under low magnification.

Other surface finishing methods that were tried
were as-machined surfaces and polished surfaces on
cylindrical rods with nominal diameters of 3.3 mm (0.13 in.).
The polishing was done by mounting the rods in a drill
press and abrading the surfaces with progressively finer

28

TABLE VI

Impact Resistance of Polished and Quenched
Silicon Carbide Impact Test Bars

Quenching Temperature		Impact Resistance(a)			
		300°K (R.T.)		1590°K (2400°F)	
°K	°F	joules	in-lb	joules	in-lb
Polished controls					
		0.496	4.42	0.336	2.97
		0.448	3.97	0.228	2.02
		0.224	1.98		
		0.161	1.43		
Average		0.332	2.95	0.282	2.50
Polished and quenched in silicone: $\eta = 350\times10^{-6}$ m²/sec					
2400	3860	0.183	1.22	0.043	0.38
		0.050	0.44	0.042	0.37
				0.028	0.25
Average		0.117	0.83	0.038	0.33

(a) Charpy impact test; 1.36 J (12 in-lb) hammer; 38.1 mm span (1.5 in.); test bars nominally 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.)

silicon carbide abrasive paper followed by a 6μm diamond paste on a piece of paper. The impact resistances of controls and quenched rods are given in Table VII.

The as-machined and the polished controls had similar high temperature impact resistances that averaged 0.0144 joules (0.128 in-lb) and 0.0138 joules (0.122 in-lb), respectively. The average room temperature impact resistance, determined only for the as-machined controls, was 0.024 joules (0.213 in-lb).

The as-machined rods, quenched from 2270°K (3630°F) in silicone fluid with a viscosity of 350x10^{-6} m^2/sec, had an average high temperature impact resistance of 0.019 joules (0.162 in-lb) and an average room temperature impact resistance of 0.027 joules (0.240 in-lb). These values, though only slightly greater than those for controls, indicate improvement in impact resistance by quenching.

The rods which were polished and quenched from 2270°K (3630°F) in silicone fluid with a viscosity of 350x10^{-6} m^2/sec had an average high temperature impact resistance of 0.060 joules (0.536 in-lb). This value represents an over four-fold increase in impact resistance. It indicated that polishing is a preferred step when hot pressed silicon carbide is to be quenched. However, the individual impact resistance values were widely scattered and this showed that a reliable technique had not yet been developed.

3. Flexural Strength Results

When fracture surfaces of quenched silicon carbide bars and rods were examined, there appeared to be significant periphereal layer of altered material. This layer was thicker when quenching from higher temperatures and when the time at a high temperature was increased. It was believed that high temperatures promoted an alteration of the surface layer that weakens it. To test this, groups of cylindrical rods were subjected to high temperatures and then cooled slowly in the furnace or more quickly in still air (but not quenched) and then tested for flexural strength at room temperature. The flexural strength was measured by four point loading using rods that were about 2.5 mm (0.10 in.) in diameter. The outer and inner span dimensions were 25.4 mm (1.0 in.) and 8.47 mm (0.33 in.) respectively.

TABLE VII

Impact Resistance of
Silicon Carbide Cylindrical Rods

Quenching Temperature		Impact Resistance[a]			
°K	°F	300°K (R.T.)		1590°K (2400°F)	
		joules	in-lb	joules	in-lb
As-machined controls					
		0.027	0.240	0.010	0.090
		0.021	0.186	0.027	0.240
				0.006	0.054
Average		0.024	0.213	0.014	0.128
Polished controls					
				0.016	0.144
				0.015	0.132
				0.024	0.210
				0.008	0.072
				0.006	0.054
Average				0.014	0.122
As-machined and quenched in silicone: $\eta = 350 \times 10^{-6}$ m²/sec					
2270	3630	0.036	0.318	0.014	0.120
		0.018	0.162	0.023	0.204
Average		0.027	0.240	0.019	0.162
Polished and quenched in silicone: $\eta = 350 \times 10^{-6}$ m²/sec					
2270	3630			0.126	1.116
				0.012	0.114
				0.043	0.378
Average				0.060	0.536

(a) Charpy impact test; 1.36 J (12 in-lb) hammer; 38.1 mm (1.5 in.) span; test rods nominally 3.3 mm (0.13 in.) diameter.

The results are shown in Figure 7. As the temperature to which the rods were subjected was increased, the room temperature strength remained about the same until the treatment temperatures were in the neighborhood of 2400°K (3860°F). Then the room temperature strength dropped rapidly as the treatment temperature was further increased.

Subsequently, rods were quenched from 2570°K (4170°F) and from lower temperatures into silicone fluid with a viscosity of 350x10-6 m²/sec. The flexural strengths of these rods were determined, as before, and the results are listed in Table VIII. Rods quenched from the highest temperature, 2570°K (4170°F) had an average strength of 447.7 MN/m² (64,930 psi) and these were weak compared to the control average strength of 544.4 MN/m² (78,960 psi). As the quenching temperature was reduced, the room temperature flexural strength of the rods increased. At a quenching temperature of 2270°K (3630°F) rods had an average strength of 680.4 MN/m² (98,680 psi) and this represents a 25% increase in strength. With a quenching temperature of 2220°K (3540°F) strengths were still high with an average of 672.0 MN/m² (97,470 psi).

The viscosity of the silicone was also a factor. At a quenching temperature of 2270°K (3630°F) a group of four rods quenched in silicone oil with a viscosity of 100x10⁻⁶ m²/sec had an average strength of 397.6 MN/m² (57,670 psi) and this was well below that for rods quenched from the same temperature into silicone with a viscosity of 350x10⁻⁶ m²/sec, 680.4 MN/m² (98,680 psi) as reported above.

The conclusion was drawn that temperatures higher than about 2300°K (3680°F) are to be avoided in treating this silicon carbide. Care should be taken not to hold specimens at high temperatures for any longer than necessary.

Residuals from the silicon carbide impact tests, reported in Table VII, were tested for flexural strength by three point loading on a one-half inch span. The strength values were extraordinarily high because of the less than ideal span-to-diameter ratio, 3.9:1. The average results, expressed as a percentage of the average flexural strength of the as machined controls residuals which are impact tested at room temperature, are given
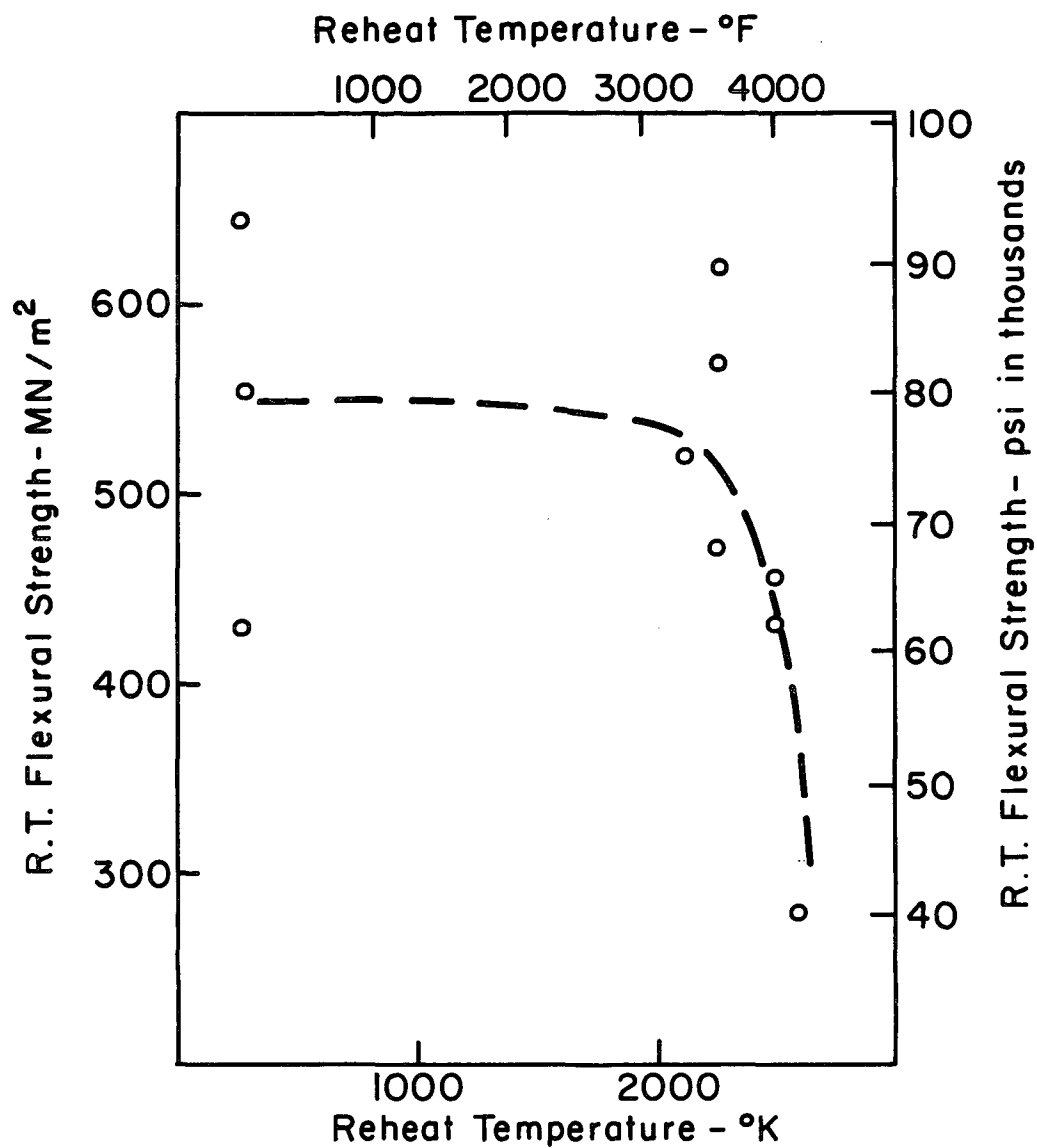
Figure 7 — Room Temperature Flexural Strength vs. Reheat Temperature for Silicon Carbide Cylindrical Rods.

TABLE VIII

Room Temperature Flexural Strength of Silicon Carbide Cylindrical Rods Quenched in Silicone ($\eta = 350 \times 10^{-6}$ m^2/sec) at Room Temperature

Quenching Temperature			Flexural Strength[a]	
			MN/m^2	PSI
Controls			431.9	62,640
			564.7	81,900
			636.7	92,340
		Average	544.4	78,960
2570°K	4170°F		289.9	42,040
			583.9	84,690
			469.3	68,070
		Average	447.7	64,930
2470°K	3990°F		607.8	88,160
			457.6	66,370
			379.6	55,050
			362.8	52,620
		Average	452.0	65,550
2370°K	3810°F		615.5	89,270
			498.1	72,240
			622.2	90,240
			409.9	59,450
		Average	536.4	77,800
2270°K	3630°F		738.2	107,070
			694.2	100,690
			608.7	88,280
		Average	680.4	98,680
2220°K	3540°F		758.7	110,040
			585.4	84,900
		Average	672.1	97,470

(a) Four point loading: outer span 25.4 mm (1.0 in.); inner span 8.47 mm (0.33 in.).

in Table IX. The results are correlated with the impact test results. That is, quenching as-machined controls gave only slightly higher flexural strengths. Greater improvement in flexural strength was obtained when polished rods were quenched. Again it was indicated that polishing is a preferred step when hot pressed silicon carbide is to be quenched.

4. Discussion

The large amount of negative slotted rod tip deflection, or slot closing, observed in the room temperature rod tests showed that quenching should be an effective means of improving the mechanical strength of hot pressed silicon carbide. The high temperature rod test indicated that the improvement can be expected to be retained at high temperatures, especially 1590°K (2400°F).

Impact tests on silicon carbide rectangular bars were disappointing. Impact resistance values for quenched bars were low. This behavior was due to thermal shock cracks which were not readily apparent. These cracks were not in a location that would be expected. They were longitudinal cracks. Their absence in small quenched cylindrical rods suggested that they occurred because of a shape dependency. The bar edges were quenched more rapidly.

The slotted impact test bar gave evidence that compressive surface forces were generated by quenching. Evidently the thermal shock damage was severe enough to nullify the effect of a compressed surface layer on the impact resistance.

The impact test results for silicon carbide cylindrical rods were more encouraging. They showed some improvement in impact resistance for quenched rods. However, even in those cases, the impact values were lower than would be expected based on tip deflections previously measured. Failure to achieve greater improvements was attributed to surface alteration. The altered layer was a dull black, and it was considered that the layer was the result of reaction with carbon monoxide. Such a reaction has been reported by Ervin[23] and it was indicated that

TABLE IX

Room Temperature Flexural Strength of Residuals
from Silicon Carbide Rod Impact Tests (Table VII)

| | Average Flexural Strength[a] | | | |
| | R.T.I.[b] | | H.T.I.[c] | |
	No. of Specimens	Percent[d]	No. of Specimens	Percent[d]
As machined controls	4	100	5	85
Polished controls			10	119
As machined and quenched[e]	4	101	3	89
Polished and quenched[e]			9	133

(a) three point loading on one-half inch span
(b) residuals from room temperature impact test
(c) residuals from high temperature impact test
(d) flexural strength as percentage of flexural strength of as machined controls residuals from room temperature impact test
(e) quenched from $2270°K$ ($3630°F$) in silicone fluid:
$\eta = 350 \times 10^{-6}$ m^2/sec

the reaction proceeds rapidly above 1570°K (2370°F) and it is favored in atmospheres containing low partial pressures of oxygen. The quenching furnace was graphite, insulated with carbon black, and both of these would tend to generate carbon monoxide. This was also true when purging was done; purging lowered the partial pressure of oxygen and encouraged the formation of carbon monoxide rather than carbon dioxide.

The flexural strength results correlated quite closely with the impact resistances. The strength increases by quenching were low but taken along with the similar impact test results, they gave additional evidence of the improvement in mechanical strength of hot pressed silicon carbide by quenching.

The impact resistances and flexural strengths of polished controls were not impressive compared to as machined controls. What was significant was that the quenching process was much more effective when cylindrical rod specimens were polished. This effect was masked by the severe thermal shock cracks in polished and quenched impact test rectangular bars. Since the effectiveness of quenching rod specimens seemed to depend on the surface layer alteration it is conjectured that polishing made a smoother, more regular surface that offered fewer sites for reaction with gaseous compounds.

In general, it was concluded that quenching did improve the mechanical properties of hot pressed silicon carbide. To be effective, specimens to be quenched should have a polished, high quality surface and quenching schedules should be selected to minimize surface alteration by high temperature reactions with gases such as air and carbon monoxide.

The thermal shock cracks might be avoided by judicious selection of the shape of the specimen to be quenched and by quenching schedules that minimize the initial tensile stresses without reducing the plasticity or creep of the silicon carbide. It was shown that only a few hundred degrees lowering in quenching temperature improved the process and this suggests that quenching from even higher temperatures into molten salts may be an effective technique.

C. Beta Silicon Carbide Surface Layers on Silicon Carbide

Silicon carbide formed by chemical vapor deposition is predominantly β-silicon carbide[20] whereas, generally, hot pressed silicon carbide is predominantly α-silicon carbide. The coefficient of thermal expansion of the β-phase is higher than that of the α-phase at temperatures above 1000°K (1340°F).[21] Compressive stresses form at 1590°K (2400°F) in surface layers of β-silicon carbide vapor deposited at lower temperatures on α-silicon carbide because of the thermal expansion difference.

1. Experimental Procedure

Silicon carbide surface layers were formed on silicon carbide bodies by chemical vapor deposition. Dimethyldichlorosilane and hydrogen were used for the reactants. The reaction was conducted in a cylindrical graphite chamber enclosed in a shell of vitreous silica at a pressure slightly above atmospheric pressure. The graphite served as the heating element and it was inductively powered.

2. Rod Test Results

A layer 43 μm thick was deposited in 15 min. at 1300°K (1880°F) on a cylindrical rod of silicon carbide.

When the rod test was conducted at room temperature the slot, 28.6 mm x 0.305 mm (1.25 in. x 0.012 in.) opened 15 μm (0.0006 in.) indicating that surface tensile forces were present at room temperature. This same slotted rod was subjected to a high temperature rod test in which the rod was first heated to 1590°K (2400°F) and the slot width was measured as the rod cooled to room temperature. At 1590°K (2400°F) the slot had opened about 50 μm and as the rod cooled the slot closed until it reached its original value at room temperature. This behavior is shown in Figure 8.

Slot opening at room temperature is the expected result. However slot closing with increasing temperature is the predicted result whereas the opposite was observed.

A layer 86 μm thick was deposited in 30 min. at 1480°K (2200°F) on another cylindrical rod of silicon carbide.

Figure 8 – Rod Test Tip Deflection as a Function of Temperature for Silicon Carbide Rod Coated with Silicon Carbide by Chemical Vapor Deposition at 1300°K (1880°F).

When the rod test was conducted at room temperature the slot, 28.6 mm x 0.305 mm (1.125 in. x 0.012 in.) closed 101 μm (0.004 in.) indicating that rather strong surface compressive forces were present at room temperature. This slotted rod was subjected to the high temperature rod test twice. In the first run the rod was heated at 0.3° to 0.4°K sec^{-1} (0.54° to 0.72°F sec^{-1}) to 1670°K (2550°F). The slot width changed very little until the temperature reached 1500°K (2240°F) and then it opened rapidly.

On cooling to room temperature, the slot closed to a width considerably less than its original value. In a second high temperature rod test, the rod was heated at 0.2° to 0.3°K sec^{-1} (0.36° to 0.54°F sec^{-1}) to 1700°K (2600°F). Again the slot width changed very little until the temperature reached 1500°K (2240°F) and then it opened rapidly. However, even at the highest temperature the slot was still smaller than the original value at room temperature. These high temperature rod test results are shown in Figure 9. The results with this second rod test indicated that the surface layer was in compression at all temperatures from room temperature to 1650°K (2510°F).

Examination of this slotted rod after the two high temperature rod test cycles revealed that the slot surfaces were laced with cracks, that some melted phase had formed on the silicon carbide rod, and that some phase had grown in bubble-like formations on the chemical vapor deposited silicon carbide surface layers. It was also evident that the surface layer had separated from the rod at numerous places. These observations are depicted in Figures 10 and 11.

Room temperature and high temperature rod tests were conducted also with an as-machined, untreated silicon carbide rod. In both cases the slotted rod tips did not deflect in either direction. With some materials, slot machining causes alteration of the slot surfaces which yields movement apart of the rod tips. This can cause observation of anomalous behavior if it is not accounted for. However, rod tip deflection due only to slot machining was not observed in the hot pressed silicon carbide of this work.

3. Impact Test Results

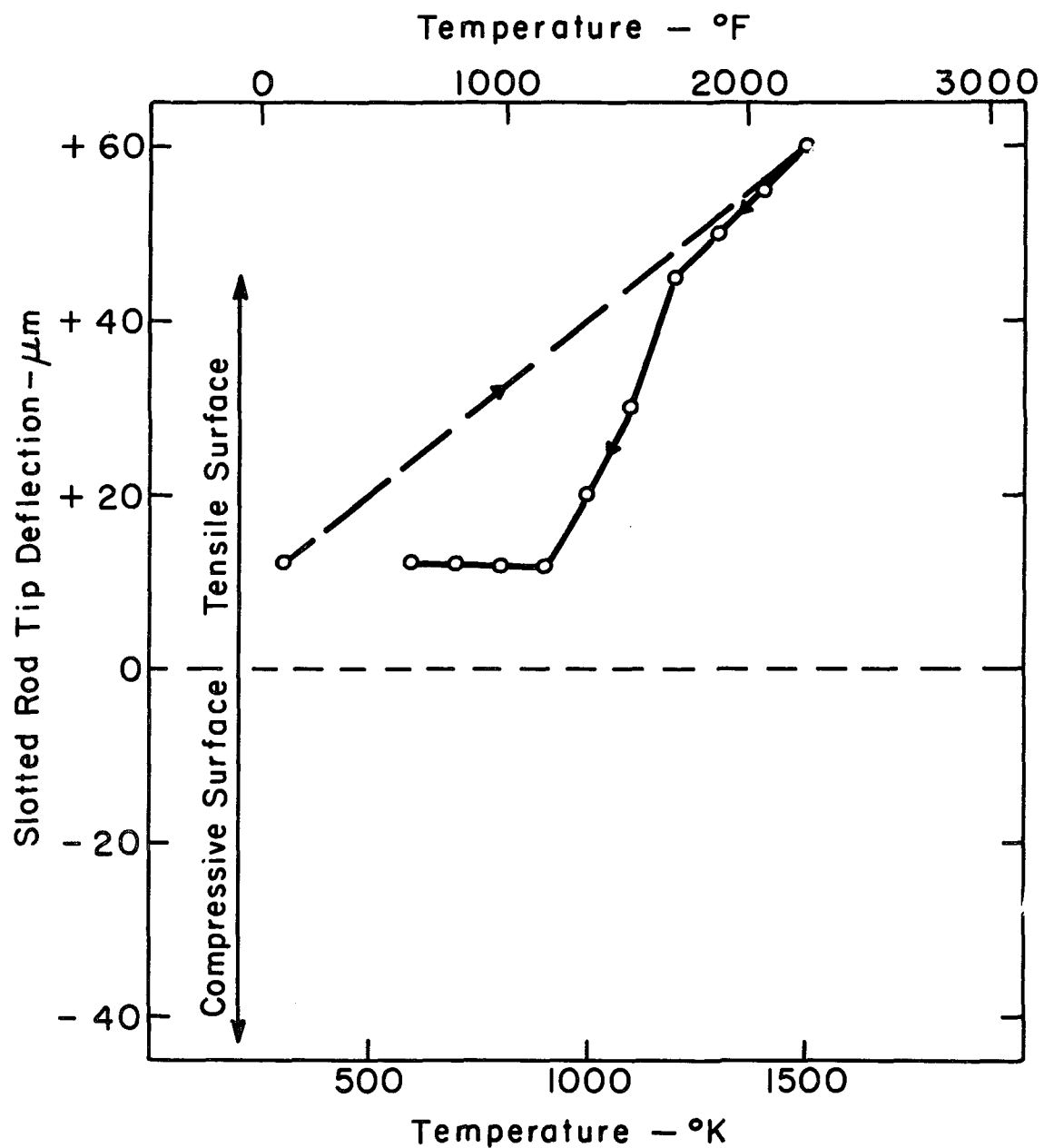Rectangular impact test bars of silicon carbide were coated with silicon carbide by chemical vapor

40
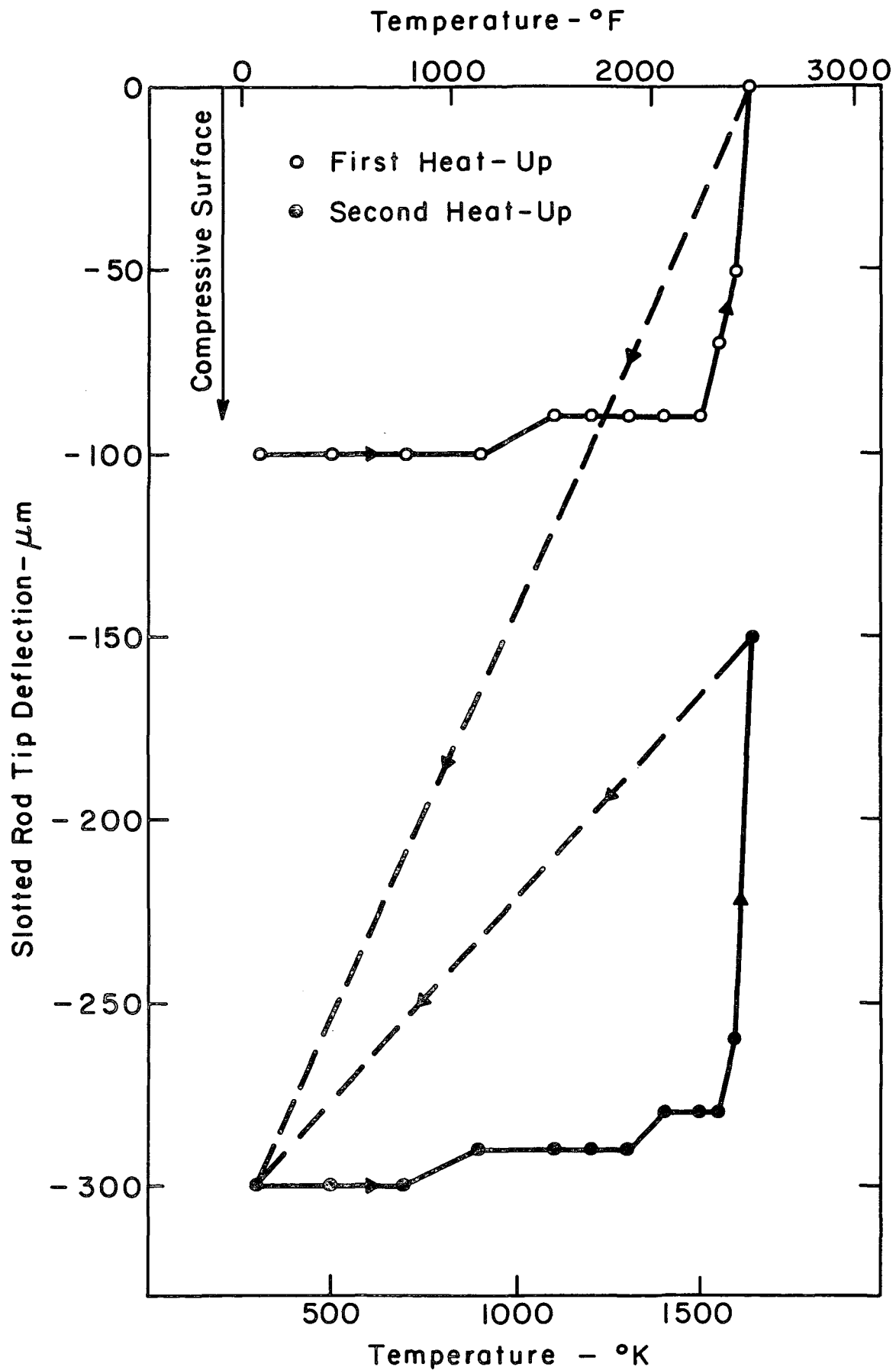
Figure 9— Rod Test Tip Deflection as a Function of Temperature for
Silicon Carbide Rod Coated with Silicon Carbide by Chemical
Vapor Deposition at 1480 °K (2200 °F)

41
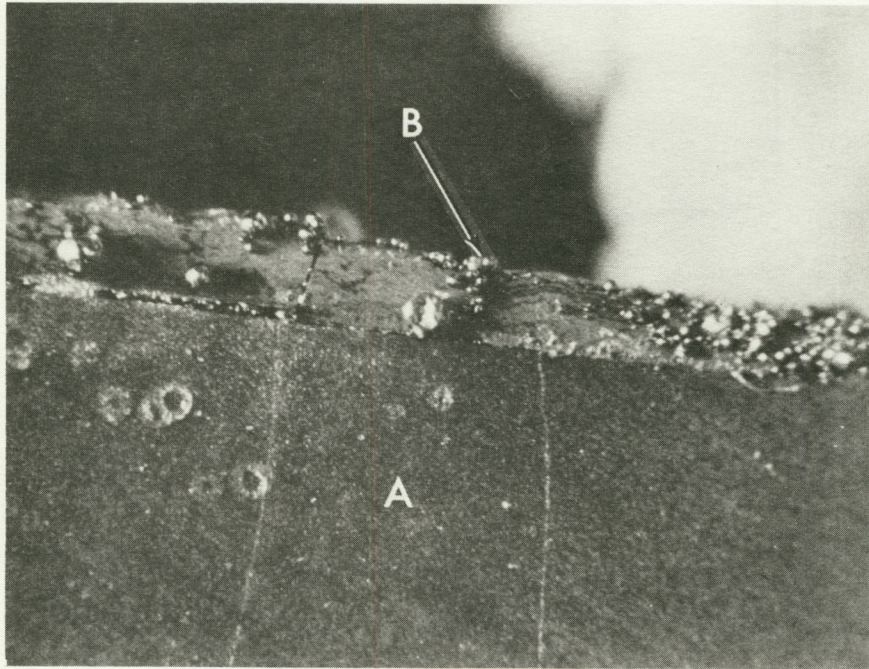
Figure 10 – Section of High Temperature Rod Test Specimen (A) Slot Surface. The slot surface exhibits many cracks. The glassy rings are evidence of a melted phase having formed on the silicon carbide rod. (B) Bubble like formations have grown on the chemical vapor deposited silicon carbide surface layer and the surface layer has separated at places from the rod. (Mag: 26 X).
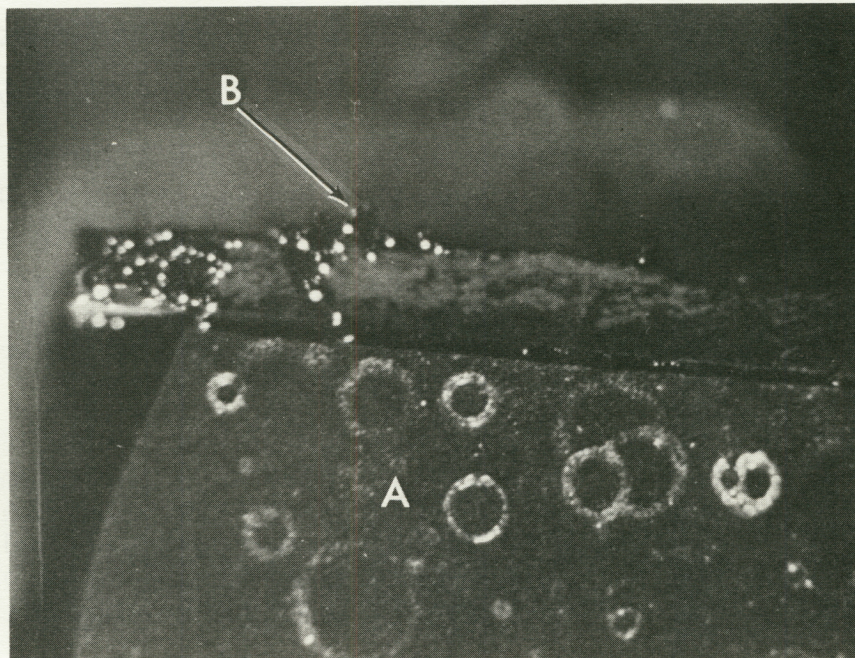
Figure II – Section of High Temperature Rod Test Specimen, (A) Slot
Surface. Glassy rings are evident on the silicon carbide
rod . (B) Bubble – like formations on the chemical
vapor deposited silicon carbide surface layer. The
surface layer has separated from the rod and it is seen
that the bubble – like phase has grown at the interface
and in a crack in the surface layer.

43

deposition at 1480°K (2200°F). Each bar was treated individually by coating for an interval with the reactant flow in one direction along its axis and then the bar was turned end-for-end and coating was continued for an equal interval. More uniform coatings were obtained in this manner.

A number of impact tests of coated bars and control bars (not coated, as-machined) were conducted. The results are given in Table X. The controls had an average impact resistance of 0.333 joules (2.95 in-lb) at room temperature and 0.280 joules (2.48 in-lb) at 1590°K (2400°F). Two bars coated with CVD silicon carbide had impact resistances of 0.224 joules (1.98 in-lb) and 0.229 joules (2.02 in-lb). Obviously, the impact resistance of the silicon carbide at 1590°K (2400°F) was not improved by chemical vapor deposited silicon carbide surface layers. This lack of success obviated testing coated bars at room temperature.

There were no indications on the coated impact test bars of cracking, a melted phase, or bubble-like formations as observed on the high temperature rod test specimen. Part of the coating near a fracture surface separated during the impact test; this indicates low adhesion between the chemical vapor deposited silicon carbide and the silicon carbide bar.

4. Discussion

The various phenomena observed in the high temperature rod test specimen are probably responsible for the strength and inconsistent test behavior of the rods. One can only speculate about these phenomena and the magnitude of the effects. In the first place, it seems likely that the SiC coatings were not single phase. It has been reported[20] that silicon carbide formed by chemical vapor deposition from an organosilane below 1670°K (2550°F) tends to have excess silicon and, furthermore, there is a tendency for such material to contain unreacted carbon. Excess silicon would increase the thermal expansion of a vapor deposited layer; thus, higher tensile surface forces would be generated upon cooling. Consequently, the coating would be likely to crack. Excess carbon could increase or decrease the thermal expansion depending on its physical form.

Excess silicon or carbon could contribute to the formation of new phases during the high temperature rod

44

TABLE X

Impact Resistance of Hot Pressed Silicon Carbide Rectangular Bars
with Chemical Vapor Deposited Silicon Carbide Surface Layers

Charpy impact test; 1.36 J (12 in-lb) hammer; 38.1 mm (1.5 in.) span
[bars nominally 6.35 mm.x 6.35 mm.x 57.2 mm.
(0.25 in. x 0.25 in. x 2.25 in.)]

Impact Resistance

Surface Layer Thickness	300°K (R.T.)*		1590°K (2400°F)	
	Joules	In-lb	Joules	In-lb
Controls	0.519	4.60	0.286	2.53
	0.146	1.30	0.220	1.95
			0.490	4.33
			0.127	1.12
			0.353	3.12
			0.244	2.16
			0.255	2.26
			0.266	2.35
Average	0.333	2.95	0.280	2.48
CVD Silicon Carbide Surface Layers				
157 μm			0.224	1.98
96.5 μm			0.229	2.02

* These results were obtained with a 2.71 J (24 in-lb) hammer. Experience indicates that results with this hammer are apparently similar to those for the 1.36 J (12 in-lb) hammer.

45

tests. These new phases, or at least the bubble-like
phase observed on the coating, apparently grow in cracks
and at interfaces and so create a wedging action which
leads to further cracking and to separation of the
surface layer from the rod. The difference in behavior
between the rod coated at 1300°K (1880°F) and the rod
coated at 1480°K (2200°F) probably arises because of
differences in excesses of silicon and carbon at the
two temperatures.

Similar phenomena were not observed in the impact
test bars because a freshly cut or fractured surface
was not exposed to a high temperature for an extended
period.

This method of improving the impact resistance of
silicon carbide ceramics is tentatively rejected. It
should be remembered however that the method has not been
disproven and that chemical vapor deposited silicon
carbide surface layers of better quality may yet be
beneficial.

D. Random Silicon Carbide Surface Layers on Oriented
       Silicon Carbide

This method requires forming an oriented body of
α-silicon carbide with a-axes parallel to the surface.
If a randomly oriented silicon carbide layer is placed
on this body at high temperatures, the surface would be
in compression at 1590°K (2400°F) because of the greater
thermal contraction of the underlying body (a-axis) than
that for the surface layer.

1. Procedure

Chemical vapor deposited silicon carbide was placed
on hot pressed silicon carbide at 1480°K (2200°F).
Dimethyldichlorosilane and hydrogen were used as reactants.
The deposition chamber was described in a previous section.

2. Results and Discussion

Some x-ray diffraction patterns were obtained from
the vapor deposited silicon carbide, hot pressed silicon
carbide, and on hot pressed silicon carbide that had been
powdered.

46

As-received hot pressed silicon carbide had diffraction peaks whose relative intensities were not in the same order as those listed in the card files; also these peaks were not in the same order as the powdered silicon carbide pattern. The changes in order were minor suggesting that there may have been a slight degree of preferred orientation in the hot pressed material.

The vapor deposited silicon carbide gave broad, diffuse diffraction peaks, in order of intensity (CuKα); $2\theta = 35.9$ {004}, $2\theta = 60.3$ {110}, $2\theta = 72.0$ {114}, and $2\theta = 75.7$ {202}. Other diffraction peaks, characteristic of silicon carbide, were missing. The shape of the peaks, broad and diffuse, indicated that the deposited layer was fine grained or poorly crystallized. The relative order of intensity of the peaks was the same as that for the hot pressed material so there were no indications of a significant degree of preferred orientation in the deposited layer.

The vapor deposited silicon carbide on hot pressed silicon carbide was heat treated at 1620°K (2460°F) for 30 min. and examined by x-ray diffraction. After the heat treatment the diffraction peaks were less broad and some small new peaks had appeared. Apparently, some recrystallization had occurred but there were no indications of enhanced preferred orientation.

The success of this method for improving the impact resistance of silicon carbide hangs on the ability to deposit oriented layers. The investigation gave no indication of significant preferred orientation so this method was dropped from consideration.

E.   Silicon Carbide Surface Layers on Silicon Nitride

If a silicon carbide surface layer is placed on a silicon nitride body at a low temperature, compressive stresses will form in the surface layer at higher temperatures because of the lower thermal expansion of the underlying silicon nitride than the thermal expansion of the silicon carbide surface. As cited previously,[19] over the range 290°K-1470°K (60°-2190°F) silicon carbide has a coefficient of thermal expansion of 5.0×10^{-6} m/m°K $(2.78 \times 10^{-6}$ in/in°F) whereas silicon nitride has a coefficient of thermal expansion of 2.78×10^{-6} m/m°K $(1.54 \times 10^{-6}$ in/in°F).

1. Experimental Procedures

CVD silicon carbide

Silicon carbide surface layers were formed on silicon nitride bodies by chemical vapor deposition at 1120°K (1560°F). Dimethyldichlorosilane and hydrogen were used as reactants. The deposition chamber was as described in a previous section.

Carburized silicon nitride

Another procedure involved packing silicon nitride bodies in carbon black and heating for a time. It is generally recognized that silicon nitride reacts readily with graphite dies during hot pressing and often some interlayer is provided to prevent the reaction. In this case, however, it was the intention to react the carbon with the surface layers of the silicon nitride with the expectation of forming silicon carbide.

This second process was called carburizing. The silicon nitride, packed in carbon black, was contained in a sealed refractory muffle which was either fireclay or alumina.

2. Rod Test Results

Some room temperature rod tests were conducted in order to determine what slotted rod tip deflection occurred in untreated silicon nitride specimens. As mentioned previously, with some materials, slot machining causes alteration of the slot surfaces and this can cause unexpected rod tip movement.

Silicon nitride rectangular rods were slotted with the 0.30 mm (0.012 in.) thick blade. Within experimental error, no slotted rod tip deflection occurred. In addition several silicon nitride rods were slotted with the 0.76 mm (0.030 in.) thick blade. These rods had an average deflection of +48 μm (0.0019 in.); that is, the rod tips moved apart 48 μm giving a false indication of tensile surface forces. This amount was subtracted from all tip deflection results obtained from rods slotted with the 0.76 mm (0.030 in.) blade. This false indication of tensile surface forces occurs because the damage to the slot surfaces increases the volume that this material tends to occupy forcing the rod tips apart.

CVD silicon carbide

A cylindrical silicon nitride rod, coated with silicon carbide by chemical vapor deposition at 1120°K (1560°F) was

subjected to a rod test at room temperature (0.30 mm blade, no surface alteration correction). The slotted rod tips moved apart 25.4 μm (0.001 in.) and this indicated that tensile surface forces had been present as expected.

This same slotted rod was subjected to a high temperature rod test in which the rod was heated to 1630°K (2470°F) and then the deflection of the slotted rod tips was measured as the rod cooled slowly. The data obtained are shown in Figure 12. The potential of the method was amply demonstrated; tensile surface forces existed at room temperature and they diminished as the temperature increased. At temperatures above 1120°K (1560°F), the vapor deposition temperature, the surfaces were in the desired condition, that is, acted upon by compressive forces.

Also shown in Figure 12 is a curve which gives the locus of points of rod tip deflection as a function of temperature. The points were calculated from expansion data cited by Lynch, et al,[19] and by Kirchner[21] using equations given by Gruver and Buessem.[22] The calculation was made using 100°K (180°F) intervals and values of the differential thermal expansion, $\frac{1}{a}\frac{da}{dt}$, for that interval. Undetermined constants in the equations were estimated by assuming that the room temperature rod tip deflection was accurate and then computing a factor to account for these constants and to make the calculated curve agree with the deflection observed at room temperature.

The curve in Figure 12 illustrates the positive deflection at low temperature to be expected because of the expansion differences. It also shows the relatively smaller deflection to be expected at elevated temperatures due to diminishing differences between the differential expansions as temperature increases. For instance, the differential thermal expansion of silicon carbide at 400°K (260°F) is 3.9×10^{-6} m/m°K (2.17×10^{-6} in/in°F) while that for silicon nitride is 1.6×10^{-6} m/m°K (0.89×10^{-6} in/in°F). At 1500°K (2240°F) the differential expansion of silicon carbide is 5.3×10^{-6} m/m°K (2.94×10^{-6} in/in°F) whereas that for silicon nitride is 4.9×10^{-6} m/m°K (2.72×10^{-6} in/in°F). Therefore temperature changes in the neighborhood of 1500°K (2240°F) will lead to small thermal stresses but similar changes in the neighborhood of 400°K (260°F) will lead to considerably larger thermal stresses.

The plotted experimental data roughly followed the calculated curve at low temperatures. At high temperatures
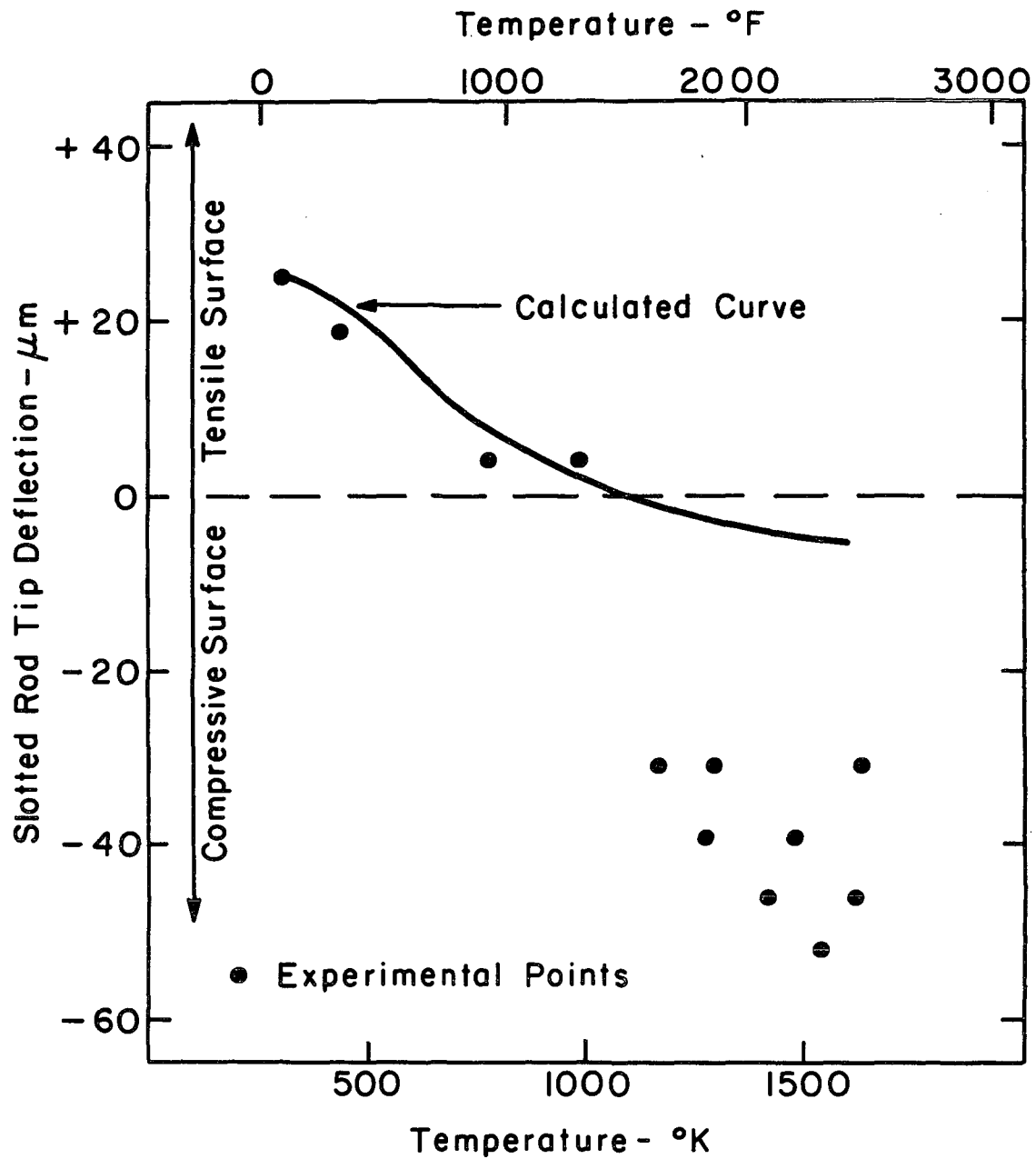
Figure 12— Rod Test Tip Deflection as a Function of Temperature for Silicon Nitride Rod Coated with Silicon Carbide by Chemical Vapor Deposition at 1120°K (1560°F).

there were large deviations. These were largely due to
experimental error in that at a red heat slot edges
become less distinguishable. The tendency was to see a
slot as smaller than it actually is. Other errors arose
because the elastic moduli were assumed to be independent
of temperature and the thermal expansion data were from
materials not necessarily the same in composition or
character as the materials used.

Carburized silicon nitride

Room temperature rod test data from carburized
rectangular silicon nitride rods [nominally: 6.35 mm
x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.)]
are given in Table XI. Specimens carburized at 1400°K
(2060°F) in alumina muffles had tensile surface forces
at room temperature as shown by the rod test data. The
greatest slot deflection observed in this group was
developed after 48 hours treatment. Increasing the
treating period reduced the tensile surface stresses.

Specimens carburized at 1410°K (2080°F) in fireclay
muffles had tensile or compressive surface forces. When
an activator, barium carbonate, was added to the carbon
black, tensile forces were generated at room temperature.
Without the activator, compressive surface forces were
generated at room temperature. The source of the
compressive forces was suggested by the slotted rod
behavior of an oxidized specimen that was heated at the
same temperature but in the furnace ambient rather than
packed in carbon black. Apparently the oxidized surface
had a thermal expansion lower than that for silicon
nitride and compressive surface forces were generated
at room temperature. Such surfaces may have a beneficial
effect on mechanical strength of silicon nitride at low
temperatures but the desired result was tensile surface
stresses at room temperature that become compressive
stresses at 1590°K (2400°F).

One rod carburized at 1550°K (2330°F) without an
activator in a fireclay muffle had compressive surface
forces which were the same as those for a rod oxidized
on the same schedule. It was believed that the perme-
ability to air of the porous fireclay muffle led to
oxidation rather than carburization and thus compressive
surface forces were generated at room temperature.

One of the carburized silicon nitride rods that had
exhibited tensile surface forces at room temperature was

TABLE XI

Room Temperature Rod Tests on Carburized Silicon Nitride Rectangular Rods

Positive deflection indicates tensile surface forces, negative deflection indicates compressive surface forces.

Treatment	Slotted Rod Tip Deflection(a)
Carburized: 1400°K (2060°F)-48 h, alumina muffle	+0.043 mm
Carburized: 1400°K (2060°F)-72 h, alumina muffle	+0.018
Carburized: 1400°K (2060°F)-101 h, alumina muffle	+0.010
Carburized: 1410°K (2080°F)-16 h, alumina muffle with 1% BaCO₃ activator	+0.035
Carburized: 1410°K (2080°F)-16 h, alumina muffle with 3% BaCO₃ activator	+0.028
Oxidized: 1410°K (2080°F)-16 h, in ambient	-0.015
Carburized: 1410°K (2080°F)-16 h, fireclay muffle	-0.015
Carburized: 1550°K (2330°F)-24 h, fireclay muffle	-0.078
Oxidized: 1550°K (2330°F)-24 h, in ambient	-0.086

(a) All deflection values are standardized for slot width, length, and specimen dimensions and corrected for deflection of untreated control material, when applicable.

52

subjected to a high temperature rod test in which the slotted rod tip deflection was measured while heating slowly to 1630°K (2470°F). The data, shown in Figure 13, show that the tensile surface force at room temperature was converted to a compressive surface force at high temperatures. The scatter of the data prohibits determining the temperature at which the stress changes sign but it is evident that the surface stress was compressive at 1590°K (2400°F).

3. Impact Test Results

CVD silicon carbide

Impact test bars of silicon nitride were coated with silicon carbide by chemical vapor deposition at 1250°K (1790°F). Each bar was treated individually by coating for an interval with the reactant flow in one direction along its axis and then the bar was turned end-for-end and coating was continued for an equal interval. More uniform coatings were obtained in this manner.

Coated bars and control bars were impact tested at 1590°K (2400°F). The results are listed in Table XII. The silicon nitride controls had an average impact resistance of 0.500 joules (4.43 in-lb) at room temperature and an average impact resistance of 0.465 joules (4.11 in-lb) at 1590°K (2400°F).

One silicon nitride bar with a 32 μm layer of chemical vapor deposited silicon carbide had an impact resistance of 0.429 joules (3.80 in-lb); another with a 76 μm layer of silicon carbide had an impact resistance of 0.234 joules (2.07 in-lb); a third with a 137 μm layer of silicon carbide had an impact resistance of 0.188 joules (1.67 in-lb). The chemical vapor deposited silicon carbide layers did not improve the impact resistance of the silicon nitride. Indeed, it appeared that the thicker the vapor deposited layer was, the lower the impact resistance of the coated silicon nitride was.

Carburized silicon nitride

Impact test bars of silicon nitride were carburized at various temperatures in fireclay and alumina muffles and subsequently impact tested at 1590°K (2400°F).

The impact resistances of silicon nitride bars carburized in fireclay muffles are given in Table XIII.

Figure 13 – Rod Test Tip Deflection at Various Temperatures for Silicon
Nitride Carburized at 1410 °K (2080 °F) in an Alumina Muffle
with 3% $BaCO_3$ Activator.
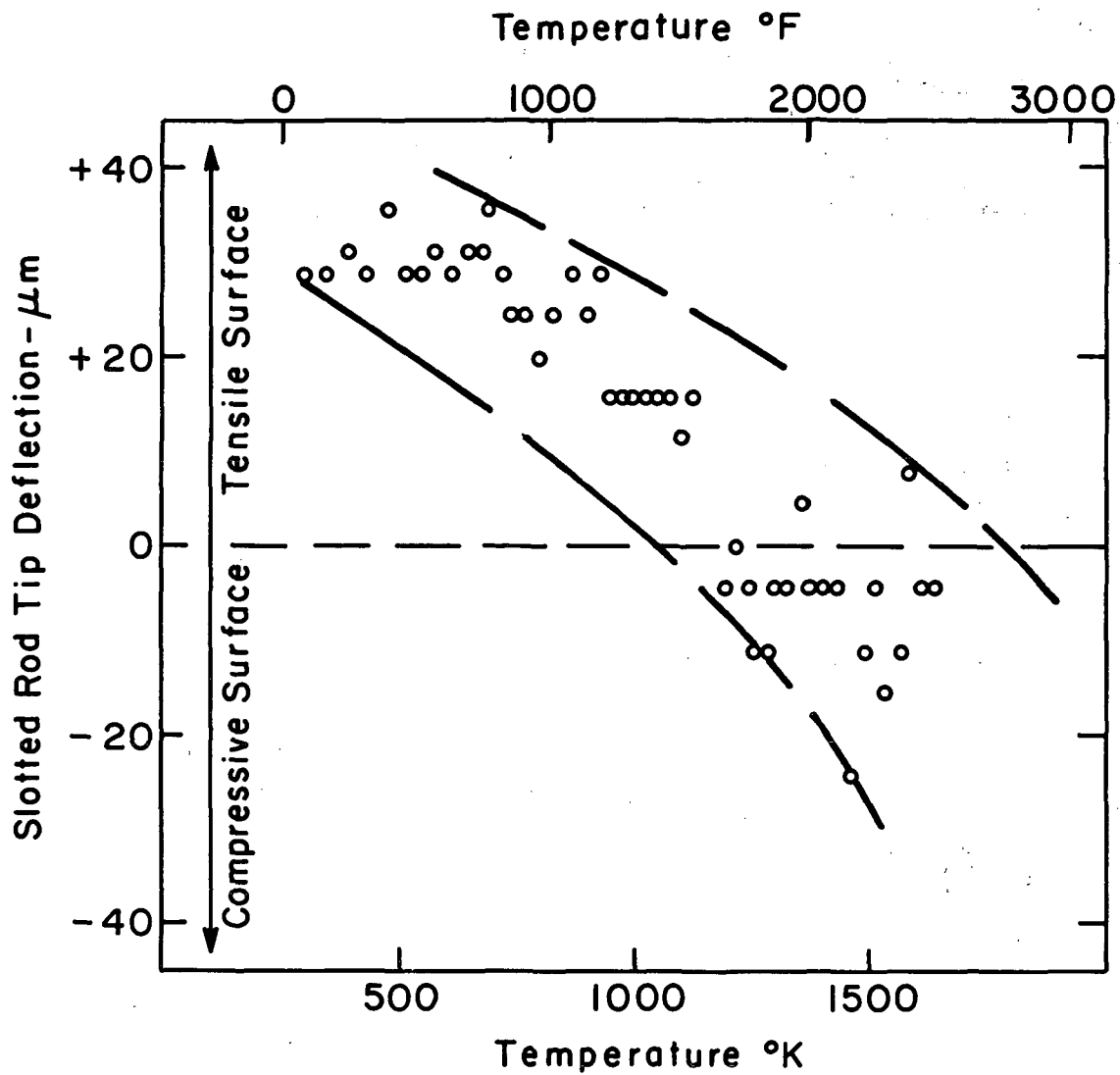
TABLE XII

Impact Resistance of Silicon Nitride with Chemical
Vapor Deposited Silicon Carbide Surface Layers

Treatment	Impact Resistance(a)			
	300°K (R.T.)		1590°K (2400°F)	
	Joules	In-lb	Joules	In-lb
Controls	0.358	3.17	0.473	4.18
	0.599{b}	5.30	0.321	2.84
	0.542(b)	4.80	0.533	4.72
			0.531(b)	4.69
Average	0.500	4.43	0.465	4.11
32 μm silicon carbide CVD at 1250°K (1790°F)			0.429	3.80
76 μm silicon carbide CVD at 1250°K (1790°F)			0.234	2.07
137 μm silicon carbide CVD at 1250°K (1790°F)			0.188	1.67

(a) Charpy impact test; 1.36 J (12 in-lb) hammer except as noted; 38.1 mm (1.5 in.) span; test bars nominally 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.)

(b) Impact test as in (a) but with a 2.71 J (24 in-lb) hammer.

TABLE XIII

Impact Resistance of Silicon Nitride Carburized in Fireclay Muffles

Treatment	Impact Resistance(a)			
	300°K (R.T.)		1590°K (2400°F)	
	Joules	In-lb	Joules	In-lb
Controls	0.358	3.17	0.473	4.18
	0.599(b)	5.30	0.321	2.84
	0.542(b)	4.80	0.533	4.72
			0.531(b)	4.69
Average	0.500	4.43	0.465	4.11
Carburized: 1200°K (1700°F)-24 h			0.549	4.86
			0.521	4.61
Carburized: 1300°K (1880°F)-24 h			0.527	4.66
			0.450	3.98
Carburized: 1400°K (2060°F)-24 h			1.041	9.22
			0.971	8.60
Carburized: 1400°K (2060°F)-24 h			0.188(b)	1.67
			0.376(b)	3.32
Carburized: 1410°K (2080°F)-46 h			0.332	2.94

(a) Charpy impact test; 1.36 J (12 in-lb) hammer except as noted; 38.1 mm (1.5 in.) span; test bars nominally 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.)

(b) Impact test as in (a) but with . 2.71 J (24 in-lb) hammer.

In most cases the impact resistance of the silicon nitride was not improved. However, one group of two carburized at 1400°K (2060°F) for 24 hours had significantly greater impact resistances, 1.041 joules (9.22 in-lb) and 0.971 joules (8.60 in-lb). The average impact resistance of the controls was 0.465 joules (4.11 in-lb) and so the carburized group were more than twice as strong as the controls. In fact the two values represent attainment of the short range goal of six inch-pounds at 1590°K (2400°F).

For obscure reasons, repeating the carburizing schedule with other impact test bars did not reproduce the high impact resistance values. It was conjectured that one reason may have been lack of control of oxygen in the carburizing process; another reason may have been bar surfaces with non-uniform damage due to machining. α-cristobalite occurs more readily on bars carburized in a fireclay muffle than those carburized in an alumina muffle.

The impact resistances of silicon nitride bars carburized in alumina muffles are given in Table XIV. Again, in most cases the impact resistance of the silicon nitride was not improved. However, one group of two carburized at 1400°K (2060°F) for 48 hours had high impact resistances of 0.876 joules (7.75 in-lb) and 0.526 joules (4.66 in-lb). The first value represents a significant increase in resistance over the average value for the controls, 0.465 joules (4.11 in-lb), and, again, attainment of the short range goal of six inch-pounds.

4. Analyses By X-Ray Diffraction

Surfaces of carburized silicon nitride have been examined by x-ray diffraction. Usually there were diffraction peaks that corresponded to those from α-cristobalite; the relative quantities of α-cristobalite present did not correlate with impact resistance. No diffraction peaks corresponding to silicon carbide were identified. This may have been due to the near overlap of diffraction peaks from silicon nitride and silicon carbide. Some distinct and relatively intense new diffraction peaks were detected but these also did not appear to correlate with impact resistance. The source of these diffraction peaks is unknown.

5. Flexural Strength Results

Residuals from the impact test bars that had been carburized at 1400°K (2060°F) for 24 hours and that had an impact resistance of 0.971 joules (8.60 in-lb) were cut up to yield slabs with one surface an original surface of the bar. The flexural strengths of these slabs with

TABLE XIV

Impact Resistance of Silicon Nitride Carburized in Alumina Muffles

Treatment	Impact Resistance(a)			
	300°K (R.T.)		1590°K (2400°F)	
	Joules	In-lb	Joules	In-lb
Controls	0.358(b)	3.17	0.473(b)	4.18
	0.599	5.30	0.321(b)	2.84
	0.542	4.80	0.533(b)	4.72
			0.531	4.69
Average	0.500	4.43	0.465	4.11
Carburized: 1400°K (2060°F)-16 h			0.430	3.18
			0.470	4.16
Carburized: 1400°K (2060°F)-48 h			0.526	4.66
			0.876	7.75
Carburized: 1400°K (2060°F)-72 h			0.523	4.68
Carburized: 1400°K (2060°F)-101 h			0.355	3.14
			0.598	5.29

(a) Charpy impact test; 2.71 J (24 in-lb) hammer except as noted; 38.1 mm (1.5 in.) span; test bars nominally 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.)

(b) Impact test as in (a) but with 1.36 J (12 in-lb) hammer.

the original surface in tension were determined by three
point loading on a one-half inch span. Similar slabs
from an untreated control were also cut and tested.
The slabs were approximately 1.3 mm (0.05 in.) thick and
6.35 mm (0.25 in.) wide.

Three carburized slabs had an average flexural
strength of 639.1 MN/m^2 (92,700 psi); four controls had
an average flexural strength of 526.8 MN/m^2 (76,400 psi).
Thus the treated slabs were 21% stronger than the controls.
The coefficient of variation for these results was 18%;
consequently the flexural strength by itself was not
conclusive evidence for improvement by carburization.
However taken with the rod test results and the impact
test results, it was strong evidence that carburization
improved the mechanical strength of hot pressed silicon
nitride.

6. Discussion

The rod test results from the silicon nitride
cylindrical rod that was coated with silicon carbide by
chemical vapor deposition demonstrated that this approach
to improving the impact resistance is correct and
potentially useful. The poor impact test results from
rectangular silicon nitride bars with silicon carbide
surface layers were probably due to deficiencies in the
composition and structure of the chemical vapor deposited
layers. As mentioned earlier, chemical vapor deposition
of silicon carbide at low temperatures tends to yield
deposits which have excess or unreacted silicon and
carbon. Excesses of silicon would tend to increase the
thermal expansion, excesses of carbon may either increase
or decrease the thermal expansion which would, however,
still be higher than that for silicon nitride. Thus
such excesses would affect the amount but not the direction
of rod test results. They would, however, decrease the
mechanical integrity of the silicon carbide surface
layers.

The rod test results, the impact resistance results,
and the flexural strength results from carburized silicon
nitride combine to yield very strong evidence that this
approach to improving the mechanical strength of hot
pressed silicon nitride is valid. Inconsistencies in
rod test results arose probably because of lack of full
control of the carburization process. The carburization
process must compete with oxidation of the silicon nitride.
X-ray diffraction results from carburized surfaces did
not indicate the anticipated silicon carbide but its presence

is not yet ruled out. In addition to cristobalite, some other new phase or composition was evident but not identified. Consequently carburization of silicon nitride is not well understood and control of the process must await further explanation.

These same considerations apply to the impact resistance values of carburized silicon nitride. Another likely factor in the impact tests was the condition of the machined surfaces. The silicon nitride bars were used as-machined with no further surface finishing. The machining was done manually with a diamond cut-off wheel and it was likely that variations such as the wear of the diamond wheel, the feed rate, and the depth of cut caused variations in surface condition. The surfaces were smooth and reflective and defects were not seen by optical microscopic examination. Hence surface variations were on a small dimensional scale and they were expected to contribute to only ordinary variations in strength. However it is surmised now that the mechanical strength of hot pressed silicon nitride is critically dependent on even the submicroscopic surface finish.

V.   SUMMARY AND CONCLUSIONS

Two candidate materials for future development for use in gas turbine engines are hot pressed silicon carbide and hot pressed silicon nitride. These materials, though brittle and, consequently, deficient in impact resistance, have high mechanical strength and oxidation resistance at expected turbine operating temperatures. Therefore the merits of these materials make it worthwhile to try to overcome their limitations.

In well made polycrystalline ceramics fracture originates at surface flaws. Compressive surface layers are effective in raising the nominal stress at which these surface flaws act to cause failure, thus increasing the mechanical strength of the materials.

Attempts were made to form compressive surface layers on hot pressed silicon carbide and hot pressed silicon nitride at 1590°K (2400°F) in order to improve their impact resistance at that temperature.

60

Silicon nitride surface layers were formed on silicon carbide at high temperatures. The lower thermal expansion of silicon nitride should place the surface layers in compression at lower temperatures. Layer formation was attempted by chemical vapor deposition, pack nitriding, nitriding vapor deposited silicon, and reaction sintering of silicon-silicon nitride coatings. Compressive surface forces were generated in the layers formed by chemical vapor deposition and by pack nitriding. However, the surface layers in all cases were not well developed and impact tests were not conducted. Nonetheless the attractive potential of this method remains. Developments in process control should lead to the desired results.

High compressive surface forces were generated in silicon carbide by quenching. However the high temperatures involved led to thermal shock fracture and alteration of surface layers through reaction with air or carbon monoxide. The thermal shock fracture could be avoided in small cylindrical rods and improved impact resistance and flexural strength were obtained. The altered surface layer was believed to be responsible for less than expected improvements. Polishing was found to be a desired procedure when silicon carbide was to be quenched. Judicious selection of the quenching process variables, specimen size and shape, and the severity of quench should allow this method to be very effective in improving the high temperature impact resistance of hot pressed silicon carbide.

Chemical vapor deposited layers of silicon carbide were placed on hot pressed silicon carbide at a temperature below 1590°K (2400°F). At higher temperatures, the deposited layers would be expected to be in compression due to their greater thermal expansion. Although the desired surface stress was detected in one instance, the test procedure gave inconsistent results. Other phases in the vapor deposited silicon carbide is believed to be the explanation. Impact resistances of silicon carbide bars with chemical vapor deposited silicon carbide layers were not improved. This method is tentatively rejected. However, vapor deposited silicon carbide layers of better quality may yet be beneficial.

The possibility of using the thermal expansion difference of the a-axis and the c-axis of α-silicon carbide to form compressive surface layers was studied. This method

required the chemical vapor deposition of silicon carbide with preferred orientation. Since a significant degree of preferred orientation in deposited layers was not detected, this method was dropped from consideration.

Silicon carbide surface layers were formed on silicon nitride by chemical vapor deposition. Another process, call carburizing, that is, reacting silicon nitride surfaces with carbon, was also tried. In both instances compressive surface forces were detected at 1590°K (2400°F). The chemical vapor deposited layers did not improve the high temperature impact resistance. Carburizing did improve the high temperature impact resistance and the short range goal of six inch pounds impact resistance was surpassed in three instances. However the impact resistance values were inconsistent with some being lower than control values. The carburizing process did not lead to detectable silicon carbide on the surfaces but some other new, unidentified phase(s) or composition was detected. Consequently, the carburizing process is not well understood and consistent improvement in impact resistance must await further explanation of the process.

VI.   APPENDIX A

IMPACT RESISTANCE OF VARIOUS
SILICON CARBIDE AND SILICON NITRIDE CERAMICS

At the request of the Project Manager the impact resistances of a number of other silicon carbide and silicon nitride ceramics were determined. The impact specimens were standard rectangular impact test bars as described in the main text (6.35 mm x 6.35 mm x 57.2 mm [0.25 in. x 0.25 in. x 2.25 in.]). The results are listed in Table XV, together with similar results for Norton hot pressed silicon carbide machined at Ceramic Finishing Company.

TABLE XV

Impact Resistance of Various Silicon Carbide and
Silicon Nitride Rectangular Bars

Material[a]	Impact Resistance[b]			
	300°K (R.T.)		1590°K (2400°F)	
	Joules	In-lb	Joules	In-lb
A. Norton hot pressed silicon carbide	0.387	3.43	0.302	2.68
	0.226	2.00	0.277	2.45
B. Hot pressed silicon nitride[a]	0.256	2.26	0.203	1.79
	0.230	2.04	0.186	1.65
C. Self-bonded silicon carbide[a]	0.087	0.77	0.054	0.47
	0.087	0.77	0.050	0.44
D. SiC-Si-C composite[a]	0.047	0.42	0.041	0.36
	0.047	0.42	0.047	0.42

(a) Identification of these materials may be obtained from the Project Manager.

(b) Charpy impact test; 1.36 J (12 in-lb) hammer, 38.1 mm (1.5 in.) span; bars nominally 6.35 mm x 6.35 mm x 57.2 mm (0.25 in. x 0.25 in. x 2.25 in.).

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